ANALYSIS OF ISSUES SURROUNDING THE USE OF SPRAY ADJUVANTS WITH HERBICIDES

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This paper is intended to serve as a source document for basic information concerning adjuvants commonly used with herbicides. Its intended audience is interdisciplinary team members who are responsible for the analysis of projects that consider the use of these adjuvants. It is not a risk assessment, although it does provide some hazard information. It should be used in conjunction with existing national herbicide risk assessments.

The paper consists of five parts. The first section is an introduction to the more common adjuvants used by the Forest Service in herbicide applications, grouped by type. The second part is a listing of common herbicide formulations and the accompanying adjuvant recommendations. The sources of this information are the herbicide labels. The third section lists the ingredients of the adjuvants described in Section 1. This information is from a variety of sources, including labels, MSDS's, manufacturer's product information, or studies involving the materials. In some cases the ingredients cannot be specifically identified. The fourth section gives a brief description of the hazard of the ingredients listed in Section 3, by adjuvant, including two tables that list the results of standard acute toxicity testing in mammals and aquatic species. The fifth section is a set of 5 discussions involving various aspects of surfactants that might be of use in environmental analysis.

Table of Contents

1. Introduction

Adjuvants are spray solution additives that are mixed with an herbicide solution to improve performance of the spray mixture. Adjuvants can either enhance activity of an herbicide's active ingredient (activator adjuvant) or offset any problems associated with spray application, such as adverse water quality or wind (special purpose or utility modifiers). Activator adjuvants include surfactants, wetting agents, sticker-spreaders, and penetrants. This paper deals mainly with commonly used activator adjuvants used in herbicide applications in forestry.

Adjuvants are not under the same registration guidelines as are pesticides. The U.S. Environmental Protection Agency (U.S. EPA) does not register or approve the labeling of spray adjuvants, although the California Department of Pesticide Regulation (DPR) does require the registration of those adjuvants that are considered to increase the action of the pesticide it is used with. All adjuvants are generally field tested by the manufacturer with several different herbicides against many weeds, and under different environments. Surfactants, or surface-acting agents, are a broad category of activator adjuvants that facilitate and enhance the absorbing, emulsifying, dispersing, spreading, sticking, wetting, or penetrating properties of herbicides.

1. Wetter/Spreaders

Wetter/Spreaders are most often used with herbicides to help it spread over and penetrate the waxy cuticle (outer layer) of a leaf or to penetrate through the small hairs present on the leaf surface. Because of the high surface tension of water, spray mixture droplets can maintain their roundness and sit on the leaf hairs or waxy surface without much of the herbicide actually contacting the leaf. The primary purpose of a wetter/spreader is to reduce the surface tension of the spray solution to allow more intimate contact between the spray droplet and the plant surface. They may also act to change the permeability of the leaf surface.

Most wetter/spreaders used with herbicides are considered non-ionic surfactants. This means that these compounds have no electrical charge and are compatible with most pesticides. There are cationic (positive charge) and anionic (negative charge) surfactants, but they are not as commonly used, with the exception of the cationic surfactant in the Roundup® formulation of glyphosate. Wetter/spreaders have the physical characteristics of both oil and water. Most wetter/spreader molecules contain a water-loving (hydrophilic) head and a long-chain hydrocarbon oil-loving (lipophilic) tail.

There are several different basic chemistries of wetter/spreaders. Examples of each[1]:

<u>Ethoxylated fatty amines</u> (Cationic)
    Entry™ II (Monsanto Company)
    POEA - Roundup® has 15% POEA

<u>Alkylphenol ethoxylate-based wetter/spreaders</u> (non-ionic)
    R-11® Spreader Activator (Wilbur-Ellis Company)

[1] The use of product names is for illustrative purposes only and is not intended as a recommendation for use or an endorsement of these products by the USDA Forest Service.

Activator 90 (Loveland Products)
X-77® (Loveland Products)
Pro-Spreader Activator (Target Specialty Products, Inc.)
Latron AG-98™ (N) (Dow AgroSciences LLC)
Latron AG-98™ (Dow AgroSciences LLC)

These surfactants usually include an alcohol as a solvent (isopropanol (Pro-Spreader Activator, AG-98™), butanol (R-11®, AG-98™ (N)), glycol (AG-98™ (N), Activator 90)), a silicone defoamer (polydimethylsiloxane), and water.

Alcohol ethoxylate-based wetter/spreaders (non-ionic)

Activator N.F. (Loveland Products) – may no longer be available

Silicone-Based wetter/spreaders

Also known as organosilicones, these are increasing in popularity because of their superior spreading ability. This class contains a polysiloxane chain. Some of these are a blend of non-ionic surfactants (NIS) and silicone while others are entirely silicone. The combination of NIS and a silicone surfactant can increase absorption into a plant so that the time between application and rainfall can be shortened. This is known as rainfastness. The surfactants extreme spreading ability may lead to droplet coalescence and subsequent runoff if applied at inappropriately high rates.

Examples:

Sylgard® 309 (Wilbur-Ellis Company) –silicones
Freeway® (Loveland Products) –silicone blend
Dyne-Amic® (Helena Chemical Company) - silicone blend
Silwet L-77® (Loveland and Helena) – silicones
Kinetic (Helena Chemical Company) – silicone blend

Blends normally include an alcohol ethoxylate, a defoamer, and propylene glycol.

Sticker/Spreaders

A sticker can perform three types of functions. It can increase the adhesion or "stickiness" of solid particles that otherwise might be easily dislodged from a leaf surface. It can also reduce evaporation of the pesticide. The third function can be to provide a waterproof coating. Many of the stickers contain surfactants as their principal functioning agent and are sold as spreader-stickers, which give both a sticker action and a wetter-spreader action. These will perform the first two functions quite well. But since the surfactants that provide wetter-spreader action must be somewhat water soluble, they may not provide good protection from rain. This will be provided by products that contain latex (rubber), polyethylene (plastic), resins (rosin), polymenthenes (rosin-like), or other waterproofing agents.

Bond® Spreader Sticker Deposition Aid (Loveland Products)
Tactic™ Sticker – Organosilicone surfactant – deposition agent (Loveland Products)

R-56® Spreader Sticker (Wilbur-Ellis Co.)
Cohere® Nonionic Spreader Sticker (Helena Chemical Co.)

Oils

Adjuvants that are primarily oil-based have been gaining in popularity especially for the control of grassy weeds. Oil additives function to increase herbicide absorption through plant tissues and increase spray retention. They are especially useful in applications of herbicides to woody brush or tree stems to allow for penetration through the bark. Oil adjuvants are made up of either petroleum, vegetable, or methylated vegetable or seed oils plus an emulsifier for dispersion in water.

Vegetable Oils – The methylated seed oils are formed from common seed oils, such as canola, soybean, or cotton. They act to increase penetration of the herbicide. These are comparable in performance to crop oil concentrates. In addition, silicone-seed oil blends are also available that take advantage of the spreading ability of the silicones and the penetrating characteristics of the seed oils.

The U.S. Food and Drug Administration (FDA) considers methyl and ethyl esters of fatty acids produced from edible fats and oils to be food grade additives (CFR 172.225). Because of the lack of exact ingredient statements on these surfactants, it is not always clear whether the oils that are used in them meet the U.S. FDA standard.

MSO® Concentrate Methylated Seed Oil (Loveland Products)
Hasten® (Wilbur-Ellis Company)
The surfactant in Pathfinder™ II (a triclopyr formulation)
Improved JLB Oil Plus (Brewer International)
Cide-Kick and Cide-Kick II (Brewer International)
Cygnet Plus Spray Adjuvant (Brewer International)

Blends of vegetable oils and silicone-based surfactants

Syl-tac™ (Wilbur-Ellis Company)
Phase™ (Loveland Products)

Crop Oils and Crop Oil Concentrates - These are normally derivatives of paraffin-based petroleum oil. Crop oils are generally 95-98% oil with 1-2% surfactant/emulsifier. Crop oils also promote the penetration of a pesticide spray. Traditional crop oils are more commonly used in insect and disease control than with herbicides. Crop oil concentrates are a blend of crop oils (80-85%) and a nonionic surfactant (15-20%). The purpose of the nonionic surfactant in this mixture is to emulsify the oil in the spray solution and lower the surface tension of the overall spray solution.

kerosene (found in the triclopyr formulation Garlon 4),
Agri-dex® (Helena Chemical Co. or Setre Chemical Co.)
Red-Top Mor-Act® (Wilbur-Ellis Company)
Herbimax (Loveland Products)

Fertilizer/Surfactant Mixtures

Nitrogen fertilizers (ammonium sulfate and ammonium nitrate) have been added to adjuvants to increase herbicide activity. These fertilizer solutions have improved the performance consistency on some weeds. Herbicides that appear to benefit from the addition of ammonium are the relatively polar, weak acid herbicides such as glyphosate, the sulfonylureas (Oust, Escort, Telar, etc.), and the imidazolinones (Arsenal, Plateau, Chopper, etc.). Velvetleaf and some grassy annual weeds in particular have been responsive to the addition of nitrogen fertilizer in the spray mix. Some broadleaves and grasses show little or no response with the inclusion of ammonium fertilizer solutions. Ammonium-based fertilizers and, in particular, ammonium sulfate (AMS) are also being promoted to reduce potential antagonism with hard water.

First Choice® Exciter Activator (Western Farm Service)
Magnify Activator – Penetrant (Monterey AgResources)
Class Act® Next Generation (Agrilliance, LLC)
Intensify Activator/Penetrant (West Link Ag)

2. Special Purpose or Utility Adjuvants

The special purpose or utility adjuvants are used to offset or correct certain conditions associated with mixing and application such as impurities in the spray solution, extreme pH levels, and drift. These adjuvants include acidifiers, buffering agents, water conditioners, anti-foaming agents, compatibility agents, and drift control agents.

The pH of most solutions is not high or low enough for important herbicide breakdown in the spray tank. Acidifiers (example LI-700® and Tri-fol®) are sometimes recommended for use with herbicides because of greater absorption of weak acid type herbicides when the spray solution is acidic.

LI-700® Surfactant Penetrant Acidifier (Loveland Products)
Tri-fol® Acidifier and Buffering Agent (Wilbur Ellis Company)

Drift reduction agents will generally increase the average droplet size so as to reduce the amount of fine droplets that are especially susceptible to drift.

In-Place® Deposition and Drift Management Agent (Wilbur Ellis Company)
Sinker Polymer Carrier and Drift Retardant (Helena Chemical Company)

Defoamers are used to reduce the foaming that might occur during agitation of the spray mixture. They typically contain a silicone compound (dimethylpolysiloxane) as their principal active ingredient. Some also include small amounts of silicon. The silicone compound acts to reduce the surface tension of the mixture, so foaming is eliminated or reduced. The silicon particles physically burst air bubbles.

Foaminator™ Dry (Agrilliance, LLC)
No Foam (Wilbur Ellis Company)
No Foam Dry (Wilbur Ellis Company)
No Foam® B (Creative Marketing and Research)

3. Colorants

Colorants are added to an herbicide mixture prior to application so that the actual treated area can be readily determined. This helps to prevent skips and overlaps. It can also be useful for reducing human exposures to recently treated vegetation.

Examples:

Hi-Light™ Blue (Becker-Underwood, Inc.)
Colorfast® Purple (Becker-Underwood, Inc.)

References for Section 1

Curran, W.S., M.D. McGlamery, R.A. Liebl, D.D. Lingenfelter. 1999. Agronomy Fact 37 – Adjuvants for enhancing herbicide performance. Penn State College of Agricultural Sciences, Cooperative Extension. 8 pages. Accessed on-line at http://cropsoil.psu.edu/extension/facts/uc106.pdf on October 18, 2006.

Hazen, J.L. 2000. Adjuvants – Terminology, Classification, and Chemistry. *Weed Technology.* 14:773-784

McMullan, P.M. 2000. Utility Adjuvants. *Weed Technology.* 14:792-797

2. Herbicide-Surfactant combinations as recommended on herbicide labels or based on field experience

Clopyralid

- Transline™ (Dow AgroSciences) – 0.25 – 0.5% non-ionic, or use surfactant manufacturer's label (also crop oils can be used)

Glyphosate

- Glyphosate VMF (DuPont) – 0.5 – 2.5% nonionic
- Accord® Concentrate (Monsanto) – 0.5 – 2.5% nonionic
- Glypro™ (Dow AgroSciences) - >=0.5% nonionic with >50% ai
- Roundup® Original (Monsanto) – none needed (contains POEA-based surfactant)
- Accord® SP (Monsanto) – none needed (contains surfactant – not identified)

Hexazinone

- Pronone® (Pro-Serve, Inc.) – none needed (pelletized formulation)
- Velpar®, Velpar® DF, and Velpar® L (DuPont) – none needed

Imazapic

- Plateau® (BASF) – seed oil 1.5 – 2 pints/acre; post-emergence >=0.25% nonionic with >60% ai; silicone-based, as per surfactant manufacturer's label; silicone/oil blends as per surfactant manufacturer's label

Imazapyr

- Arsenal® (American Cyanamid) – hack/squirt – none needed; foliar .25 – 1% non-ionic
- Chopper® (American Cyanamid) – foliar - 12-50% seed oil or crop oil or silicone/oil blends as per surfactant manufacturer's label; hack/squirt – none needed; thinline basal or low volume basal – 100% crop oil or diesel fuel

Metsulfuron methyl

- Escort® (DuPont) – 0.25% minimum or surfactant manufacturer's rate (non-ionic with >80% ai); don't use products with acetic acid (LI-700); seed oils or seed oil/silicone blends as per surfactant manufacturer's label.

Picloram

- Tordon® 22K (DuPont) – none needed, but can add as per surfactant manufacturer's label

Sulfometuron methyl

- Oust®, Oust® XP (DuPont) – 0.25% non-ionic if needed

Triclopyr

- Garlon™ 3A (Dow AgroSciences) – for foliar, use surfactant manufacturer's label
- Garlon™ 4 (Dow AgroSciences) – foliar, 1-2 qts/ac or none; basal 95-99% oil or 8-16% Mor-Act; low vol basal, 70-80% oil; thinline, 25-50% oil; contains kerosene as surfactant.
- Pathfinder™ II (Dow AgroSciences) – none needed, includes a crop oil surfactant.

3. Ingredients of Adjuvants[2]

Ethoxylated fatty amines

Entry™ II

POEA is found in Roundup® at 15%, same ingredients as Entry™ II
No longer registered in California; may no longer be commercially available
Active Ingredients – 35%
Ethoxylated Tallow Amine 35% by weight (CAS 61791-26-2)[3] EPA list[4] 3 (amines, tallow alkyl, ethoxylated)
Inert Ingredients 65%
Water 64.5%?
Isopropylamine 0.5% (CAS 75-31-0) EPA list 3

Alkylphenol ethoxylate-based wetter/spreaders

R-11® Spreader Activator (Wilbur Ellis Company)

CA Reg. #2935-50142, WA Reg #AC-2935-50142
Active Ingredients – 90%
Nonylphenol polyethoxylate (CAS 9016-45-9), EPA List 4B
Label identifies as alkylphenol ethoxylate; older MSDS says 80%
Inert Ingredients 10%
1-Butanol (n-Butanol) (CAS 71-36-3), EPA List 4B
MSDS identifies as 10% butyl alcohol, same CAS#
Compounded silicone, dimethylpolysiloxane, EPA List 4B; <1% (antifoam)
Water

Activator 90 (Loveland Products, Inc.)

CA Reg. #34704-50034, WA Reg #34704-04001
Active Ingredients – 90%
Nonylphenol polyethoxylate (alkylphenol ethoxylate on label)
Tall oil fatty acids (CAS 61790-12-3?) EPA List 3 (emulsifier)
Alcohol ethoxylate (linear alcohol) – not further identified
Glycols (diethylene glycol EPA list 3?)
Dimethylpolysiloxane (CAS 63148-62-9), EPA list 4B

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[2] Adjuvant ingredients are not required to be disclosed as they are protected as Confidential Business Information (CBI) unless they include hazardous ingredients required to be identified on the Material Safety Data Sheet (MSDS). The listing of ingredients has been developed from the label, MSDS, manufacturer's publicly released information, or from the open literature. Formulations of these adjuvants can often change, so caution must be used in relying on this list.

[3] CAS refers to the Chemical Abstracts Service Registry identification number which is a unique numeric identifier for the stated chemical. The MSDS is the primary source for these numbers.

[4] EPA list refers to the US EPA list of pesticide inert ingredients. The most recent listing can be found on-line at http://www.epa.gov/opprd001/inerts/lists.html. The list is divided into 4 main categories, with list 1 and 2 being compounds of known toxic hazard or high priority for testing, list 4 being those considered of low hazard, and list 3 which contains those compounds where not enough information is known to place them into any of the other categories.

Inert Ingredients
Water (from MSDS)

X-77® Spreader (Loveland Products, Inc.)
CA Reg. # 34704-50044
Active Ingredients – 90%
Alkylphenol ethoxylate
Nonylphenol polyethoxylate (as per Paveglio et al, 1996; refer to page 29)
Tall oil fatty acids (CAS 61790-12-3?) EPA List 3 (emulsifier)
Alcohol ethoxylate (linear alcohol) - not further identified
2,2' dihydroxydiethyl ether (diethylene glycol, CAS 111-46-6) EPA list 3
Dimethylpolysiloxane (CAS 63148-62-9), EPA list 4B
Inerts – 10%
Water

Pro-Spreader Activator (Target Specialty Products)
CA Reg #1050775-50022
Active Ingredients – 90%
Nonylphenol polyethoxylate (CAS 9016-45-9) EPA List 4B
Label identifies as alkylphenol ethoxylate; MSDS says 66%
Isopropyl alcohol (CAS 67-63-0) EPA list 4B, 19%
Fatty acid (not further identified)

Latron AG-98® (N) (Rohm and Haas)
Not currently registered in California; may no longer be commercially available
Active Ingredients –
Nonylphenoxy polyethoxy ethanol (CAS 127087-87-0) 77-78%, EPA List 3
Inert Ingredients
Butyl alcohol (butanol) (CAS 71-36-3) 20-21%, EPA list 4B
Polyethylene glycol (CAS 25322-68-3) 2-3%, EPA list 4B

Latron AG-98® (Rohm and Haas)
No longer registered in California; may no longer be commercially available
Active Ingredients – 80-81%
Octylphenoxypolyethoxyethanol (CAS 9036-19-5), 80-81%, EPA list 4B
Inert Ingredients – 9-14%
Isopropanol (CAS 67-63-0), 4-5% by weight, EPA list 4B
Polydimethylsiloxane (CAS 63148-62-9), 1-2% by weight, EPA list 4B
Water, 9-14%

Alcohol ethoxylate-based wetter/spreader

Activator N.F. (Loveland Products, Inc.)
CA Reg. # 36208-50008-AA; may no longer be commercially available
Active Ingredients – 25.25%
Primary aliphatic oxyalkylated alcohol (a linear alcohol) 25%
Dimethylpolysiloxane 0.25%, CAS 63148-62-9, EPA list 4B
Inerts 74.75%

Silicone-based wetter/spreaders

Sylgard® 309
CA Reg. # 2935-50161-AA (Wilbur-Ellis Co.)
CA Reg. # 34292-50001-AA (Dow Corning Corp.)
Active ingredients – 100%
3-(3-hydroxypropyl)-heptamethyltrisiloxane, ethoxylated acetate (CAS 125997-17-3) EPA List 4B, >60%
allyloxy polyethylene glycol monallyl acetate (CAS 27252-87-5) EPA List 3, 15-40%
polyethylene glycol diacetate (CAS 27252-83-1) EPA List 3, 1-5%

Freeway® (Loveland Products, Inc.)
CA Reg. # 34704-50031, WA Reg # 34704-04005
Active Ingredients – 100%
Silicone-polyether copolymer (not further identified) (silicone surfactant)
Alcohol ethoxylates (linear alcohol) (not further identified)
Propylene glycol (CAS 57-55-6) EPA list 4B
Dimethylpolysiloxane (CAS 63148-62-9) EPA list 4B (antifoam)

Silwet® L-77
CA Reg. # 5905-50073-AA (Helena Chemical Company)
Active Ingredients – 100%
Polyalkyleneoxide modified heptamethyltrisiloxane (CAS 27306-78-1) EPA List 4B, 84%
Allyloxypolyethyleneglycol methyl ether (CAS 27252-80-8) EPA List 4B, 16%

Kinetic Molecular Zippering Action™ Brand Nonionic wetter/spreader/penetrant
CA Reg # 5905-50087-AA
Active Ingredients – 99%
Polyakyleneoxide modified polydimethylsiloxane, not further identified
Polyoxyethylene-polyoxypropylene copolymer (CAS 9003-11-6) (Poloxalene) EPA list 4B (non-ionic surfactant)
Polyoxypropylene oleate butyl ether (CAS 37281-78-0) EPA list 3, likely being used as an antifoam agent, a minor component

Sticker/Spreaders

Bond® Spreader Sticker Deposition Aid (Loveland Products, Inc.)
CA Reg # 34704-50033
Active Ingredients – 55%
Synthetic latex – 45%
Alcohol ethoxylate (primary aliphatic oxyalkylated alcohol) – 10%, a linear alcohol with unspecified carbon chain length.

Tactic™ Sticker – Organosilicone surfactant – deposition agent (Loveland Products, Inc.)
CA Reg # 34704-50041
Active Ingredients – 63.4%

Synthetic latex
1,2-propanediol (propylene glycol, CAS 57-55-6) EPA list 4B
alcohol ethoxylate (a linear alcohol with unspecified carbon chain length)
silicone polyether copolymer

R-56® Spreader Sticker (Wilbur-Ellis Co.)
CA Reg # 2935-50144
Active Ingredients – 73%
Alpha-(p-nonylphenyl)-2-hydroxypoly (oxyethylene) 40% (nonylphenol polyethoxylate nonionic surfactant? CAS 9016-45-9?) EPA List 3
Poly (methylene p-nonylphenoxy) Polyoxypropylene propanol 33%, (organic polymers, sticker?) EPA List 3

Cohere® Nonionic Spreader Sticker (Helena Chemical Co.)
CA Reg # 5905-50083-AA
Active Ingredients – 88%
Alkanolamine surfactants (unspecified; most commonly used forms in surfactants are ethanolamine (CAS 141-43-5, EPA List 3), triethanolamine (CAS 121-44-8, EPA List 2))
Alkylaryl polyethoxyethanol sulfates (unspecified)
1,2-propanediol (propylene glycol, CAS 57-55-6) EPA list 4B

Oils

MSO® Concentrate Methylated Seed Oil (Loveland Products, Inc.)
CA Reg. # 34704-50029, WA Reg #34704-04009
Active Ingredients – 100%
Methylated soybean seed oil (methyl ester soyate)
Alcohol ethoxylate (CAS 34398-01-1) EPA List 3
Tall oil fatty acids (CAS 61790-12-3) EPA list 3

Hasten® (Wilbur-Ellis Co.) (may be soon available as Competitor)
CA Reg. # 2935-50160, WA Reg #2935-02004
Active Ingredients – 100%
Ethyl oleate (CAS 111-62-6) (esterified vegetable oil) A regulated food additive under 21 CFR 172.515
Polyoxyethylene dialkylester
Sorbitan alkylethoxylate ester (not further identified)

Pathfinder™ II surfactant
In the triclopyr formulation, Pathfinder™ II, EPA Reg. #62719-176
"naturally occurring non-petroleum diluent", not identified except that it is on EPA List 4

Improved JLB Oil Plus (Brewer International)
CA Reg. # - not necessary for CA registration, as per DPR, not a surfactant but a diluent
Active Ingredients – 90%
Natural Vegetable Oils (not identified further)
Limonene (CAS 138-86-3) EPA List 3

Label indicates it includes Cide-Kick®, so may contain nonylphenol polyethoxylate

Cide-Kick® (Brewer International)
Not currently registered in California
Active ingredients – 100%
Nonylphenol polyethylene glycol ether (CAS 127087-87-0) EPA list 3, 10%
d-limonene (CAS 5989-27-5) EPA list 4B, 90%

Cide-Kick® II™ (Brewer International)
Not currently registered in California
Active ingredients – 100%
d-limonene (CAS 5989-27-5) (p-menthadienes), EPA list 4B
Terpene hydrocarbon (CAS 68956-56-9 EPA List 3?)
Nonylphenol polyethylene glycol ether (CAS 127087-87-0) EPA list 3

Cygnet Plus Spray Adjuvant for Pesticides (Brewer International)
CA Reg # 1051114-50001-AA
Active Ingredients – 100%
d,l-limonene and related isomers (90%) (CAS 5989-27-5) (p-menthadienes), EPA list 4B
Terpene hydrocarbon (CAS 68956-56-9, hydrocarbons, terpene processing by-products) EPA List 3
Alkyl hydroxypoly oxyethylene 10% (CAS 127087-87-0) nonylphenol polyethoxylate EPA List 3

Vegetable Oils and Silicone Blends

Syl-tac™ (Wilbur-Ellis Co.)
CA Reg. # 2935-50167, WA Reg #2935-00004
Active Ingredients – 100%
A blend of Hasten® and Sylgard® 309:
3-(3-hydroxypropyl)-heptamethyltrisiloxane, ethoxylated acetate (CAS 125997-17-3) EPA List 4B
Allyloxy polyethylene glycol monallyl acetate (CAS 27252-87-5) EPA List 3
Polyethylene glycol diacetate (CAS 27252-83-1) EPA List 3
Ethyl oleate (CAS 111-62-6) (esterified vegetable oil) A regulated food additive under 21 CFR 172.515
Polyoxyethylene dialkylester
Nonylphenol polyethoxylate

Phase™ (Loveland Products, Inc.)
CA Reg. # 34704-50037, WA Reg #34704-05007
Active Ingredients – 100%
Methylated esters of fatty acids (methyl ester soyate, a methylated seed oil)
Polyether modified polysiloxane
Alcohol ethoxylate

Dyne-Amic® (Helena Chemical Company)
CA Reg. # 5905-50071-AA

Active Ingredients – 99%
- Polyalkyleneoxide modified polydimethylsiloxane, not further identified (silicone surfactant)
- Alkylphenol ethoxylates (not further identified, likely is nonylphenol polyethoxylate)(non-ionic surfactant)
- Methyl esters of C16-C18 fatty acids (not further identified, but described as a highly refined methylated vegetable oil)
- Polyoxypropylene oleate butyl ether (CAS 37281-78-0) EPA list 3, likely being used as an antifoam agent, a minor component
- Polyoxyethylene-polyoxypropylene copolymer (CAS 9003-11-6) (Poloxalene) EPA list 4B, also likely being used as an antifoam agent, a minor component

Crop Oils and Crop Oil Concentrates

Kerosene, deodorized
- In the triclopyr formulation, Garlon 4, CA Reg. #62719-40-ZB
- CAS 8008-20-6, EPA List 3 (between 1 and 38.4% of formulation)

Agri-dex® (Helena Chemical Co.)
- CA Reg. # 5905-50094
- Active Ingredients – 99%
  - A mixture of heavy and light range paraffin base petroleum oils (CAS 64741-88-4, 64741-89-5), 82%
  - Polyol fatty acid esters and polyoxyethylated polyol fatty acid esters (not identified further) 17%, EPA list 3 (surfactant/emulsifier)
- Inert Ingredients – 1%

Red-Top Mor-Act® Adjuvant (Wilbur-Ellis Co.)
- CA Reg. # 2935-50098-AA
- Active Ingredients – 98%
  - Non-phytotoxic paraffin base petroleum oil 83%, CAS 8012-95-1, EPA list 3
  - Polyol fatty acid esters and polyethoxylated derivatives thereof 15%, EPA list 3 (emulsifier)
- Inert Ingredients - 2%

Herbimax® Petroleum Oil-Surfactant Adjuvant (Loveland Products, Inc.)
- CA Reg # 34704-50032
- Active ingredients – 99.3%
  - Petroleum hydrocarbons – 83%
    - light paraffinic distillate (CAS 64741-50-0) EPA List 2
    - odorless aliphatic petroleum solvent (CAS 64742-89-8, solvent naphtha) EPA List 2
  - Alkylphenol ethoxylate
  - Tall oil fatty acid (not further identified)

Fertilizer/Surfactant Mixtures

First Choice® Exciter Activator – Penetrant (Western Farm Service, Inc.)
- CA Reg # 11656-50097-AA

Active Ingredients – 51.15%
Alkyl polyglycoside (CAS 68515-73-1) EPA List 3 – corn sugar derivative, used as a wetting agent
Oligosaccharides, not further identified
Ammonium sulfate (CAS 7783-20-2) EPA List 4B, source of N fertilizer
Ammonium nitrate 9.99% (CAS 6484-52-2) EPA List 4B, source of N fertilizer

Magnify Activator – Penetrant (Monterey AgResources)
CA Reg # 17545-50018
Active Ingredients – 51.15%
Alkyl polyglycoside (CAS 68515-73-1) EPA List 3 – corn sugar derivative, used as a wetting agent
Oligosaccharides, not further identified
Ammonium sulfate (CAS 7783-20-2) EPA List 4B, source of N fertilizer
Ammonium nitrate 9.99% (CAS 6484-52-2) EPA List 4B, source of N fertilizer

Agrisolutions Class Act® Next Generation Water Conditioning Agent/Nonionic Surfactant Blend (Agrilliance, LLC)
CA Reg # 1381-50003-AA
Active Ingredients – 50.5%
Alkyl polyglycoside (CAS 68515-73-1) EPA List 3 – corn sugar derivative, used as a wetting agent
Corn syrup (CAS 8029-43-4) EPA List 4A
Ammonium sulfate 32-36% (CAS 7783-20-2) EPA List 4B, source of N fertilizer

Intensify Activator/Penetrant (West Link Ag)
CA Reg # 1051117-50005
Active Ingredients – 51.15%
Alkyl polyglycoside (CAS 68515-73-1) EPA List 3 – corn sugar derivative, used as a wetting agent
Oligosaccharides, not further identified
Ammonium sulfate (CAS 7783-20-2) EPA List 4B, source of N fertilizer
Ammonium nitrate 9.99% (CAS 6484-52-2) EPA List 4B, source of N fertilizer

Acidifiers

LI-700® (Loveland Products, Inc.)
CA Reg. # 34704-50035, WA Reg. # 34704-04007
Active Ingredients – 80%
Lecithin (phosphatidylcholine), CAS 8002-43-5, EPA list 4A (soybean lecithin base)
Propionic acid (methylacetic acid) CAS 79-09-4, 35%, EPA list 4B
Alkyl polyoxyethylene ether (likely to be ethoxylated alcohol)
Inert Ingredients – 20%
Water 20%

Tri-Fol Acidifier and Buffering Agent (Wilbur-Ellis Co.)
CA Reg # 2935-50152
Active Ingredients – 34%

Aliphatic polycarboxylate 25% (Citric Acid, CAS 77-92-9) EPA List 4A
Calcium Chloride 9% (CAS 10043-52-4) EPA List 4B

Drift Reduction Agents

In-Place® Deposition and Drift Management Agent (Wilbur-Ellis Co.)
CA Reg # 2935-50169
Active Ingredients – 100%
Amine salts of organic acids, EPA List 3
Aromatic acid, EPA List 4
Modified seed oil (not further identified except that it is on EPA List 3)
Mineral oil (not further identified except that it is on EPA List 3)

Sinker Polymer Carrier and Drift Retardant (Helena Chemical Co.)
Aquatic herbicide deposition agent
Active Ingredients - 30%
Polyacrylamide copolymers (polyvinyl polymer) (CAS 9003-05-8) EPA List 3

Defoamers

Foaminator™ Dry Antifoaming/Defoaming agent (Agrilliance, LLC)
Active Ingredients – 15.5% (Label) or 30% (MSDS)
Dimethylpolysiloxane (CAS 5989-27-5) EPA List 4B
Polypropylene glycol (CAS 25322-69-4) EPA List 4B
Silicon dioxide (CAS 7631-86-9) EPA List 4B

No Foam Defoamer (Wilbur-Ellis Co.)
CA Reg # 2935-50137
Active Ingredients – 10%
Polydimethylsiloxane (CAS 9016-00-6) EPA List 3

No Foam Dry Defoamer (Wilbur-Ellis Co.)
Active Ingredients – 10%
Polydimethylsiloxane (CAS 9016-00-6) EPA List 3

No Foam® B (Creative Marketing & Research, Inc.)
CA Reg # 1050775-50008-AA
Active Ingredients – 25%
Nonylphenol polyethoxylate (CAS 26027-38-3) EPA List 4B, 12.86% a nonionic surfactant
Ethanolamine (CAS 141-43-5) EPA List 3, approx. 4%, an anionic surfactant
Dodecylbenzene sulfonate (dodecylbenzene sulfonic acid CAS 27176-87-0) EPA List 3, 5.7%
Isopropyl alcohol (CAS 67-63-0) EPA List 4B, 2.1% (probably the foam inhibitor)
Sodium xylene sulfonate (CAS 1300-72-7) EPA List 3, <1%

Colorants and Dyes

Hi-Light™ Blue (Becker Underwood, Inc.)
All ingredients on EPA list 3 or 4A (not further identified).

Colorfast® Purple (Becker Underwood, Inc.)
With the exception of the following ingredients, listed on the MSDS, no further ingredients have been identified:
Glacial Acetic Acid (CAS 64-19-7) 23.4% by weight, EPA list 4B (solvent)
Dipropylene Glycol (CAS 25265-71-8) 1-10% by weight, EPA list 3 (solvent)
C.I.Basic Violet 3 (gentian violet) (CAS 548-62-9) 1-10% by weight, not listed by EPA (dye)

4. Hazard Assessment

Of the adjuvants discussed in this paper, only two carry the Danger signal word [5] (Entry™ II and LI-700®), which is due to the potential effects to the eyes (severely irritating or corrosive). The bulk of the remainder carry the Caution signal word, while several carry the Warning signal word (again because of potential irritant effects to the skin or eyes). None of these adjuvants carry the poison symbol. All of the adjuvants discussed here are no more than slightly toxic when ingested, inhaled, or absorbed through the skin (Acute Toxicity Categories III or IV).

The bulk of these adjuvants do not contain ingredients found on U.S. EPA's inerts list 1 or 2. This is either based on the identified ingredients, or if these ingredients are not sufficiently identified, by information given by the manufacturers. The assessment of hazards for these adjuvants is limited by the proprietary nature of the formulations. Unless the U.S. EPA classifies a compound in the formulation as hazardous, the manufacturer is not required to disclose its identity. At the current time, the disclosure of whether a material is hazardous is based primarily on acute toxicity. There are two products listed that include ingredients on U.S. EPA's inerts list 2 (Herbimax® Petroleum Oil-Surfactant Adjuvant (Loveland Products, Inc.) and In-Place® Deposition and Drift Management Agent (Wilbur-Ellis Co.).

The primary summary statement that can be made is that the more common risk factors for the use of these adjuvants are through skin or eye exposure. These adjuvants all have various levels of irritancy associated with skin or eye exposure. This points up the need for good industrial hygiene practices while utilizing these products, especially when handling the concentrate, such as during mixing. The use of chemical resistant gloves and goggles, especially while mixing, should be observed.

There is little toxicity testing done on these adjuvants. Most of the adjuvants have had some acute toxicity testing, as well as skin and eye irritation studies. The acute toxicity testing results are displayed in Table 1 for mammalian species and in Table 2 for aquatic species. 'NA' in these two tables indicates that either the particular test has not been conducted on the material, or the data was not available from the manufacturer.

Ethoxylated Fatty Amines

Entry™ II (POEA)

Danger signal word (Entry™ II); Roundup® (includes POEA) signal word is either Warning or Caution, depending upon the formulation. Skin irritant, may be allergen. Entry™ II is severely irritating to corrosive to eyes (I[6]).

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[5] Signal words are required on pesticide and registered adjuvant labels, and provide an overall view of the acute toxicity, or effects to eyes or skin, of the product. There are three signal words used by U.S. EPA, Danger, Warning, and Caution, to signify decreasing levels of this toxicity. In addition, the Danger signal word can be accompanied by the skull and crossbones symbol if the product is an acute poison. Refer to the table on Page 44.

[6] The Roman numeral refers to the US EPA toxicity category (I, II, III, or IV) with I representing the category of highest toxicity and IV being the lowest. Refer to 40 CFR 156.62.

For a comprehensive look at POEA as a surfactant in the Roundup® formulation, refer to SERA 1997a and SERA 2003a. As Entry™ II is the same formulation as the POEA surfactant in Roundup®, these same references can be used.

Entry™ II and POEA both contain ethoxylated ingredients. Ethoxylates are formed by reactions of ethylene oxide. In the manufacturing process, some unreacted ethylene oxide as well as the contaminant 1,4-dioxane can become part of the final formulation. Both of these chemicals are considered likely human carcinogens. For a comprehensive look at the risks of 1,4-dioxane in the POEA surfactant, refer to Borrecco and Neisess 1991. For a comprehensive look at the risks of ethylene oxide in ethoxylated surfactants, refer to USDA, 2003.

Alkylphenol-ethoxylate-based wetter/spreaders

R-11® Spreader Activator (Wilbur-Ellis Co.)

Caution signal word. May cause skin irritation (III). Mildly irritating to the eyes (III).

The active ingredient in R-11® Spreader Activator, nonylphenol polyethoxylate, has been linked to estrogenic effects in wildlife, including aquatic species, such as fish and amphibians. For a comprehensive look at the nonylphenol ethoxylate surfactants, refer to USDA, 2003. Butanol and compounded silicone are both on EPA list 4B. Butanol is slightly more orally acutely toxic than the nonylphenol polyethoxylate. The compounded silicone is practically non-toxic on an acute oral basis (rat LD_{50} >17 g/kg).

Activator 90 and X-77® (Loveland Products, Inc.)

Activator 90 has a Caution signal word while X-77® has a Warning signal word. Based on communications with the manufacturer, both products are fairly similar in formulation, and indeed they consider the testing data between the two to be bridgeable (S. Baker, Loveland Products, Personal Communication 6/19/02, 8/15/02). Both may cause minor skin irritation (III). Both may cause severe reddening and swelling of the conjunctiva, with possible chemical burns (II). Both did not result in skin sensitization when administered to guinea pigs. It is likely that the signal word for Activator 90 should be changed to Warning, based on its effects to the eyes.

The MSDS describes a toxicity test involving guppies (not further described). Whether this refers to the freshwater aquarium fish *Poecilia reticulata* is not known. In this acute toxicity test, the 96-hour LC_{50} was determined to be 12.7 mg/L, with a corresponding 96-hour NOEC of 5.8 mg/L. This is comparable to effects of other nonylphenol polyethoxylate-based surfactants on frogs (USDA, 2003).

One of the active ingredients, nonylphenol polyethoxylate, has been linked to estrogenic effects in wildlife, including aquatic species, such as fish and amphibians. For a comprehensive look at the nonylphenol ethoxylate surfactants, refer to USDA, 2003.

Tall oil fatty acid is a mixture of oleic, linoleic, and rosin acids derived from the hydrolysis of tall oil, a byproduct of wood pulp. Tall oil fatty acid is included in various cosmetics, such as hair dyes and bleaches, shampoos, skin cleansing preparations, and a shaving cream. Tall oil

fatty acid is approved for use as an indirect food additive. When fed to rats as 15% of the total caloric intake, tall oil fatty acid was nontoxic; however, it had a growth-retarding effect. No treatment-related effects were observed in rats fed diets containing 5% and 10% tall oil fatty acid over two generations. Liquid soap formulations containing up to 12% tall oil fatty acid did not cause dermal irritation, sensitization, or photosensitization in human subjects. One study in rats indicated that this compound had little effect on reproduction. For further information, refer to Anonymous (1989).

The compounded silicone is practically non-toxic on an acute oral basis (rat LD_{50} >17 g/kg).

Diethylene glycol is practically nontoxic with an acute oral LD_{50} value in the rat of 12.5 g/kg.

The linear alcohol is not adequately described to say anything definite about its toxicology.

Activator 90 and X-77® contain ethoxylated ingredients. Ethoxylates are formed by reactions of ethylene oxide. In the manufacturing process, some unreacted ethylene oxide as well as the contaminant 1,4-dioxane can become part of the final formulation. Both of these chemicals are considered likely human carcinogens. For a comprehensive look at the risks of 1,4-dioxane in the POEA surfactant, refer to Borrecco and Neisess 1991. For a comprehensive look at the risks of ethylene oxide in ethoxylated surfactants, refer to USDA, 2003.

<u>Pro-Spreader Activator (Target Specialty Products)</u>

Pro-Spreader Activator_has a Caution signal word. It may cause skin irritation (III) and is mildly irritating to the eyes (III).

One of the active ingredients in Pro-Spreader Activator, nonylphenol polyethoxylate, has been linked to estrogenic effects in wildlife, including aquatic species, such as fish and amphibians. For a comprehensive look at the nonylphenol ethoxylate surfactants, refer to the USDA, 2003.

Isopropyl alcohol is considered of low toxicity (acute oral LD_{50} of 5 g/kg in rat), however it is about twice as toxic as ethanol (the alcohol found in alcoholic beverages).

Pro-Spreader Activator contains ethoxylated ingredients. Ethoxylates are formed by reactions of ethylene oxide. In the manufacturing process, some unreacted ethylene oxide as well as the contaminant 1,4-dioxane can become part of the final formulation. Both of these chemicals are considered likely human carcinogens. For a comprehensive look at the risks of 1,4-dioxane in the POEA surfactant, refer to Borrecco and Neisess 1991. For a comprehensive look at the risks of ethylene oxide in ethoxylated surfactants, refer to USDA, 2003.

<u>Latron AG-98® (N) and Latron AG-98® (Rohm and Haas)</u>

Both Latron AG-98® (N) and Latron AG-98® have a Warning signal word. Latron AG-98® (N) is considered moderately irritating to the skin, based on the nonylphenol ethoxylate and butanol ingredients. Latron AG-98® is considered severely irritating to skin. Latron AG-98® (N) is severely irritating to the eyes, possibly resulting in conjunctivitis. Latron AG-98® is considered irritating to the eyes.

The active ingredients, nonylphenol polyethoxylate and octylphenol polyethoxylate, have been linked to estrogenic effects in wildlife, including fish and amphibians. For a comprehensive look at the nonylphenol ethoxylate surfactants, refer to USDA, 2003. For purposes of evaluation, the OPE surfactants can be considered equivalent to the NPE surfactants of the same ethoxylate number.

Butanol and compounded silicone (polydimethylsiloxane) are both on EPA list 4B. Butanol is slightly more orally acutely toxic than the nonylphenol polyethoxylate. The compounded silicone is practically non-toxic on an acute oral basis (rat LD_{50} >17 g/kg). Isopropyl alcohol is considered of low toxicity (acute oral LD_{50} of 5 g/kg in rat), however it is about twice as toxic as ethanol (the alcohol found in alcoholic beverages).

Latron AG-98® (N) and Latron AG-98® contain ethoxylated ingredients. Ethoxylates are formed by reactions of ethylene oxide. In the manufacturing process, some unreacted ethylene oxide as well as the contaminant 1,4-dioxane can become part of the final formulation. Both of these chemicals are considered likely human carcinogens. For a comprehensive look at the risks of 1,4-dioxane in the POEA surfactant, refer to Borrecco and Neisess 1991. For a comprehensive look at the risks of ethylene oxide in ethoxylated surfactants, refer to USDA, 2003.

Alcohol ethoxylate-based wetter/spreader

Activator N.F. (Loveland Products)

Activator N.F. has a Caution signal word. This material may irritate the skin, and may cause eye injury. Acute toxicity information was not available for this surfactant.

Activator NF contains an ethoxylated linear alcohol; however its exact composition is not specified. Several of the articles discussed in the issue questions at the end of this paper concern ethoxylated alcohols.

Compounded silicone (polydimethylsiloxane) is on EPA list 4B. The compounded silicone is practically non-toxic on an acute oral basis (rat LD_{50} >17 g/kg).

Activator NF contains ethoxylated ingredients. Ethoxylates are formed by reactions of ethylene oxide. In the manufacturing process, some unreacted ethylene oxide as well as the contaminant 1,4-dioxane can become part of the final formulation. Both of these chemicals are considered likely human carcinogens. For a comprehensive look at the risks of 1,4-dioxane in the POEA surfactant, refer to Borrecco and Neisess 1991. For a comprehensive look at the risks of ethylene oxide in ethoxylated surfactants, refer to USDA, 2003.

The large percentage of inert ingredients (74.75%) in this formulation is troublesome. It is unknown if this is all or mostly water or made up of other ingredients.

Silicone-based wetter/spreaders

Sylgard® 309 (Wilbur-Ellis Co.)

Sylgard® 309 has a Warning signal word. It is considered slightly irritating to the skin and is considered severely irritating to the eyes. It is not a skin sensitizer. Besides the acute toxicity data displayed in Table 1, the MSDS describes a 28-day oral dosing study in rats, in which rats were fed doses of 0, 33, 300, or 1,000 mg/kg/day. No significant findings of biological relevance were seen in females, while males showed some effects at highest dose (body weight gain, and changes in food consumption). This would indicate a subchronic NOEL of 300 mg/kg/day.

There has been concern expressed about the toxicity of silicone-based surfactants on terrestrial insects. Refer to issue discussion 2 on page 46.

Freeway® (Loveland Products, Inc.)

Freeway® has a Caution signal word. Freeway® is mildly or non-irritating to the skin (Category IV), and is considered slightly irritating to the eyes (Category III).

The exact identity of the silicone-based components of Freeway® is unspecified. Whether it is of the same toxicity as the active ingredient in Sylgard® 309 is unknown, however these silicone based compounds are generally of low acute toxicity.

There has been concern expressed about the toxicity of silicone-based surfactants on terrestrial insects. Refer to issue discussion 2 on page 46.

Compounded silicone (polydimethylsiloxane) is on EPA list 4B. The compounded silicone is practically non-toxic on an acute oral basis (rat LD_{50} >17 g/kg).

Propylene glycol is practically nontoxic to mammals, with an acute oral LD_{50} in rats of 20 g/mg. Propylene glycol is generally regarded as safe (GRAS) by the US Food and Drug Administration, and is an additive in foods and personal care products (21 CFR 184.1666).

Freeway® contains an ethoxylated alcohol, however its exact composition is unknown. Several of the articles discussed in the issue questions at the end of this paper concern ethoxylated alcohols.

Freeway® contains ethoxylated ingredients. Ethoxylates are formed by reactions of ethylene oxide. In the manufacturing process, some unreacted ethylene oxide as well as the contaminant 1,4-dioxane can become part of the final formulation. Both of these chemicals are considered likely human carcinogens. For a comprehensive look at the risks of 1,4-dioxane in the POEA surfactant, refer to Borrecco and Neisess 1991. For a comprehensive look at the risks of ethylene oxide in ethoxylated surfactants, refer to USDA, 2003.

Silwet L-77® (Helena Chemical Co.)

Silwet L-77® has a Warning signal word for both Loveland and Helena Chemical Company formulations. Silwet L-77® may be slightly irritating to the skin, and is not a skin sensitizer. In a repeated skin application study with rats, this material caused moderate skin irritation which resolved during a post-application recovery period. There was no evidence for cumulative or

specific organ damage to the skin or other organs, and no effect on male or female reproductive systems. It is a severe eye irritant.

Based on information on one of the MSDSs, this material is not a mutagen, based on the Ames bacterial assay and three separate mammalian assays (Chinese hamster ovary gene mutation assay, a micronucleus cytogenetic assay in mice, and in an in vitro mammalian cytogenetic test).

Findings from a 14-day dietary feeding study with rats (no dosage specified) showed that repeated high doses caused reversible adverse effects on the male and female reproductive tracts. Other effects seen were increased liver weight, altered blood cytology/chemistry, and thyroid enlargement. Evidence of partial or complete recovery was seen over a 28-day recovery period.

In addition to the acute toxicity information in Table 1, the MSDS also lists a 96-hour EC_{50} (growth) for green algae of 5.5 mg/L, with a corresponding 96-hour NOEC of 1 mg/L.

There has been concern expressed about the toxicity of silicone-based surfactants on terrestrial insects. Refer to issue discussion 2 on page 46.

Kinetic Molecular Zippering Action™ Brand (Helena Chemical Co.)

Kinetic has a Caution signal word. This material may be mildly irritating to the skin and eyes.

Kinetic is a mixture of a silicone-based surfactant and poloxalene.

The exact identity of the silicone-based components of Kinetic is unspecified. Whether it is of the same toxicity as the active ingredient in Sylgard® 309 is unknown, however these silicone based compounds are generally of low acute toxicity. There has been concern expressed about the toxicity of silicone-based surfactants on terrestrial insects. Refer to issue discussion 2 on page 46.

Poloxalene is of low toxicity on an acute oral basis, with an LD50 value in rats, mice and rabbits exceeding 3 g/kg (III). It is used as an oral veterinary treatment in cattle to cure legume bloat or as a feeding supplement to prevent bloat.

Polyoxypropylene oleate butyl ether (CAS 37281-78-0) is probably a minor component of Kinetic, used as an antifoam agent. It is a product recognized by the US Food and Drug Administration as being generally safe when used as an antifoam agent in food packaging (21 CFR 176.200).

Sticker/Spreaders

Bond® Spreader Sticker Deposition Aid (Loveland Products, Inc.)

Bond® has a Caution signal word. This material may be a slight skin irritant but is not a skin sensitizer and is a moderate eye irritant.

In addition to the aquatic toxicity test involving Daphnia shown on Table 2, the current MSDS also describes a toxicity test involving guppies (not further described). In communications with

the company this description of a toxicity test involving fish is in error and should be deleted from the MSDS. The only aquatic test with Bond® involves Daphnia as shown in Table 2.

Bond® is a mixture of synthetic latex and a linear alcohol, along with 45% inert ingredients (not otherwise specified). The exact composition of the synthetic latex is not specified; it is likely acrylic latex. The exact composition of the linear alcohol is not specified. Several of the articles discussed in the issue questions at the end of this paper concern ethoxylated linear alcohols.

The large percentage of inert ingredients (45%) in this formulation is troublesome. It is unknown if this is all or mostly water or made up of other ingredients.

<u>Tactic™ Sticker – Organosilicone surfactant – deposition agent</u> (Loveland Products, Inc.)

Tactic™ has a Caution signal word. It may be a slight skin irritant, but is not a skin sensitizer. Tactic™ is a mild to moderate eye irritant.

Tactic™ is a blend of synthetic latex and a silicone-based wetter/spreader, along with a linear alcohol. The exact composition of the synthetic latex is not specified; it is likely acrylic latex. The exact composition of the linear alcohol is not specified. Several of the articles discussed in the issue questions at the end of this paper concern ethoxylated linear alcohols.

The exact identity of the silicone-based components of Tactic™ is unspecified. Whether it is of the same toxicity as the active ingredient in Sylgard® 309 is unknown, however these silicone based compounds are generally of low acute toxicity. There has been concern expressed about the toxicity of silicone-based surfactants on terrestrial insects. Refer to issue discussion 2 on page 46.

Propylene glycol is practically nontoxic to mammals, with an acute oral LD_{50} in rats of 20 g/mg. Propylene glycol is generally regarded as safe (GRAS) by the US Food and Drug Administration, and is an additive in foods and personal care products (21 CFR 184.1666).

Tactic™ contains ethoxylated ingredients. Ethoxylates are formed by reactions of ethylene oxide. In the manufacturing process, some unreacted ethylene oxide as well as the contaminant 1,4-dioxane can become part of the final formulation. Both of these chemicals are considered likely human carcinogens. For a comprehensive look at the risks of 1,4-dioxane in the POEA surfactant, refer to Borrecco and Neisess 1991. For a comprehensive look at the risks of ethylene oxide in ethoxylated surfactants, refer to USDA, 2003.

<u>R-56® Spreader Sticker</u> (Wilbur-Ellis Co.)

R-56® has a Caution signal word. This material may be irritating to the eyes (protective eyewear is required by the label). The MSDS states that ingestion may cause nausea, but that no chronic effects are known. There is little else toxicological information on this product.

R-56® is made up of a nonylphenol polyethoxylate of unknown ethoxylate length and an organic polymer that acts as the sticker. The exact identity of this polymer is not specified.

One of the active ingredients in R-56®, nonylphenol polyethoxylate, has been linked to estrogenic effects in wildlife, including aquatic species, such as fish and amphibians. For a comprehensive look at the nonylphenol ethoxylate surfactants, refer to the USDA, 2003.

R-56® contains ethoxylated ingredients. Ethoxylates are formed by reactions of ethylene oxide. In the manufacturing process, some unreacted ethylene oxide as well as the contaminant 1,4-dioxane can become part of the final formulation. Both of these chemicals are considered likely human carcinogens. For a comprehensive look at the risks of 1,4-dioxane in the POEA surfactant, refer to Borrecco and Neisess 1991. For a comprehensive look at the risks of ethylene oxide in ethoxylated surfactants, refer to USDA, 2003.

Cohere® Nonionic Spreader Sticker (Helena Chemical Co.)

Cohere® has a Warning signal word. The label states that eye exposure causes substantial but temporary eye injury; protective eyewear is required when handling.

Cohere® is made up of anionic alkanolamine and alkylaryl sulfate surfactants, which are not further identified. The most commonly used alkanolamine forms in surfactants are ethanolamine and triethanolamine, but it is unknown whether Cohere® contains these or another form. The descriptions on the label and MSDS are insufficient to further characterize these ingredients.

Propylene glycol is practically nontoxic to mammals, with an acute oral LD_{50} in rats of 20 g/mg. Propylene glycol is generally regarded as safe (GRAS) by the US Food and Drug Administration, and is an additive in foods and personal care products (21 CFR 184.1666).

Oils

MSO® Concentrate Methylated Seed Oil (Loveland Products, Inc.)

MSO® Concentrate Methylated Seed Oil has a Caution signal word. This material may be slightly irritating to the skin and to the eyes. The product is of low acute oral and dermal toxicity (refer to Table 1).

MSO® Concentrate Methylated Seed Oil is made up of an esterified vegetable oil and a linear alcohol wetter/spreader. Based on the CAS number, the ethoxylated alcohol is an 11 carbon chain linear alcohol. Several of the articles discussed in the issue questions at the end of this paper concern ethoxylated linear alcohols.

Tall oil fatty acid is a mixture of oleic, linoleic, and rosin acids derived from the hydrolysis of tall oil, a byproduct of wood pulp. Tall oil fatty acid is included in various cosmetics, such as hair dyes and bleaches, shampoos, skin cleansing preparations, and a shaving cream. Tall oil fatty acid is approved for use as an indirect food additive. When fed to rats as 15% of the total caloric intake, tall oil fatty acid was nontoxic; however, it had a growth-retarding effect. No treatment-related effects were observed in rats fed diets containing 5% and 10% tall oil fatty acid over two generations. Liquid soap formulations containing up to 12% tall oil fatty acid did not cause dermal irritation, sensitization, or photosensitization in human subjects. One study in rats indicated that this compound had little effect on reproduction. For further information, refer to Anonymous (1989).

MSO® Concentrate Methylated Seed Oil contains ethoxylated ingredients. Ethoxylates are formed by reactions of ethylene oxide. In the manufacturing process, some unreacted ethylene oxide as well as the contaminant 1,4-dioxane can become part of the final formulation. Both of these chemicals are considered likely human carcinogens. For a comprehensive look at the risks of 1,4-dioxane in the POEA surfactant, refer to Borrecco and Neisess 1991. For a comprehensive look at the risks of ethylene oxide in ethoxylated surfactants, refer to USDA, 2003.

Hasten® (Wilbur-Ellis Co.)

Hasten® has a Caution signal word. Hasten® may be mildly irritating to the skin and to the eyes. The product is of low acute oral and dermal toxicity (refer to Table 1).

The main ingredient in Hasten® is identified in Wilbur-Ellis product information as ethylated corn, canola, and soybean oil. This is combined with sorbitan alkylethoxylate ester as a nonionic surfactant.

The polyoxyethylene dialkylester is not sufficiently identified to say anything definite about its composition or toxicity.

Recently the Hasten formulation has been changed to remove the nonylphenol polyethoxylate and replace it with a sorbitan alkylethoxylate ester. This is not further identified.

Hasten® contains ethoxylated ingredients. Ethoxylates are formed by reactions of ethylene oxide. In the manufacturing process, some unreacted ethylene oxide as well as the contaminant 1,4-dioxane can become part of the final formulation. Both of these chemicals are considered likely human carcinogens. For a comprehensive look at the risks of 1,4-dioxane in the POEA surfactant, refer to Borrecco and Neisess 1991. For a comprehensive look at the risks of ethylene oxide in ethoxylated surfactants, refer to USDA, 2003.

Pathfinder™ II surfactant (Dow AgroSciences)

Pathfinder™ II herbicide is a ready-to-use material that contains triclopyr herbicide in the butoxyethyl ester formulation combined with oil for use in treating woody plants. The surfactant is not identified except as a 'naturally occurring non-petroleum diluent'. Based on information from the manufacturer, this diluent is on EPA list 4.

Pathfinder™ II has a Caution signal word. It may cause skin irritation and slight eye irritation. From the MSDS, the 96-hour oral LD_{50} for rats is 1000 mg/kg (females), while the dermal LD_{50} for rabbits is >2,000 mg/kg. These values are not appreciably different from those for the butoxyethyl ester form of triclopyr alone. For information on the hazards and risks of using triclopyr herbicide, refer to SERA 2003b as well as U.S. EPA 1998.

Improved JLB Oil Plus (Brewer International)

Improved JLB Oil Plus has a Caution signal word. According to the manufacturer, it is exempt from California registration because the state considers it a diluent, not a surfactant. It is a mild

skin irritant, but is a severe eye irritant. If it were to be registered in California, it would perhaps be given a Warning signal word because of the severe eye irritation.

Considered a mixture of all natural oils, it is made up of natural vegetable oils (unspecified) and limonene (as a penetrant). It is intended to be used in place of diesel or kerosene in stem basal applications. Some information from the manufacturer from the early 1990's indicated the oil as being sunflower seed oil, if this is indeed what is still in the formulation, this would be considered a food-grade additive. Limonene is a derivative of plant oils, particularly lemon, orange, caraway, dill, and bergamot. It is used as a food additive in chewing gum. For a comprehensive look at the use of limonene in surfactants, refer to USDA 1992.

Cide-Kick and Cide-Kick® II™ (Brewer International)

Both Cide-Kick® and Cide-Kick® II™ have a Caution signal word. Both are considered moderately irritating to the skin. Both are considered severely irritating to the eyes and can cause redness, swelling, and chemical burns of the eye. It is likely that if these two products were registered in California, they would be assigned at least a Warning signal word.

The main ingredients in both Cide-Kick® and Cide-Kick® II™ is d-limonene. Limonene is a derivative of plant oils, particularly lemon, orange, caraway, dill, and bergamot. It is used as a food additive in chewing gum. It is insoluble in water; hence these surfactants add a water-soluble compound (nonylphenol ethoxylate) to allow for dispersion in water-based mixtures. For a comprehensive look at the use of limonene in surfactants, refer to USDA 1992. Another ingredient in Cide-Kick® II™ is an unspecified terpene hydrocarbon. This material is also a derivative of oils from botanical sources.

The solubilizer, nonylphenol polyethoxylate, has been linked to estrogenic effects in wildlife, including fish and amphibians. For a comprehensive look at the nonylphenol ethoxylate surfactants, refer to USDA, 2003.

Cide-Kick® and Cide-Kick® II™ contain ethoxylated ingredients. Ethoxylates are formed by reactions of ethylene oxide. In the manufacturing process, some unreacted ethylene oxide as well as the contaminant 1,4-dioxane can become part of the final formulation. Both of these chemicals are considered likely human carcinogens. For a comprehensive look at the risks of 1,4-dioxane in the POEA surfactant, refer to Borrecco and Neisess 1991. For a comprehensive look at the risks of ethylene oxide in ethoxylated surfactants, refer to USDA, 2003.

Cygnet Plus Spray Adjuvant for Pesticides (Brewer International)

Cygnet Plus has a Caution signal word. Cygnet Plus is considered moderately irritating to the skin and severely irritating to the eyes. A California DPR document indicates there may also be a methylated vegetable oil included although the label and MSDS do not indicate this.

The main ingredient in Cygnet Plus is d-limonene. Limonene is a derivative of plant oils, particularly lemon, orange, caraway, dill, and bergamot. It is used as a food additive in chewing gum. It is insoluble in water; hence these surfactants add a water-soluble compound (nonylphenol ethoxylate) to allow for dispersion in water-based mixtures. For a comprehensive look at the use of limonene in surfactants, refer to USDA 1992. Another ingredient in Cygnet

Plus is an unspecified terpene hydrocarbon. California DPR documents indicate this may be a methylated vegetable oil.

The solubilizer, nonylphenol polyethoxylate, has been linked to estrogenic effects in wildlife, including fish and amphibians. For a comprehensive look at the nonylphenol ethoxylate surfactants, refer to USDA, 2003.

Cygnet Plus contains ethoxylated ingredients. Ethoxylates are formed by reactions of ethylene oxide. In the manufacturing process, some unreacted ethylene oxide as well as the contaminant 1,4-dioxane can become part of the final formulation. Both of these chemicals are considered likely human carcinogens. For a comprehensive look at the risks of 1,4-dioxane in the POEA surfactant, refer to Borrecco and Neisess 1991. For a comprehensive look at the risks of ethylene oxide in ethoxylated surfactants, refer to USDA, 2003.

Vegetable Oils and Silicone Blends

Syl-tac™ (Wilbur-Ellis Co.)

Syl-tac™ has a Caution signal word. It may cause slight skin and eye irritation. Syl-tac™ is of low acute oral and dermal toxicity (refer to table 1). Syl-tac™ is a mixture of two other products (Hasten® and Sylgard® 309). Refer to the discussions of those two products.

Phase™ (Loveland Products, Inc.)

Phase™ has a Caution signal word. It may cause skin and eye irritation.

The exact identity of the silicone-based components of Phase™ is unspecified. Whether it is of the same toxicity as the active ingredient in Sylgard® 309 is unknown, however these silicone based compounds are generally of low acute toxicity. There has been concern expressed about the toxicity of silicone-based surfactants on terrestrial insects. Refer to issue discussion 2 on page 46.

Phase™ contains an ethoxylated linear alcohol, however its exact composition is not specified. Several of the articles discussed in the issue questions at the end of this paper concern ethoxylated alcohols.

Phase™ contains ethoxylated ingredients. Ethoxylates are formed by reactions of ethylene oxide. In the manufacturing process, some unreacted ethylene oxide as well as the contaminant 1,4-dioxane can become part of the final formulation. Both of these chemicals are considered likely human carcinogens. For a comprehensive look at the risks of 1,4-dioxane in the POEA surfactant, refer to Borrecco and Neisess 1991. For a comprehensive look at the risks of ethylene oxide in ethoxylated surfactants, refer to USDA, 2003.

Dyne-Amic® (Helena Chemical Co.)

Dyne-Amic® has a Caution signal word. Dyne-Amic® is mildly or non-irritating to the skin (Category IV), and may be slightly irritating to the eyes (Category IV).

Dyne-Amic® is a mixture of a silicone-based surfactant, esterified vegetable oil, and an alkylphenol ethoxylate; however the exact formulation of these ingredients is unknown. It is likely that the alkylphenol ethoxylate is nonylphenol ethoxylate, but that is not certain.

There are two CAS numbers on the label, one that corresponds to polyoxypropylene oleate butyl ether, while the other indicates poloxalene.

The exact identity of the silicone-based components of Dyne-Amic® is unspecified. Whether it is of the same toxicity as the active ingredient in Sylgard® 309 is unknown, however these silicone based compounds are generally of low acute toxicity. There has been concern expressed about the toxicity of silicone-based surfactants on terrestrial insects. Refer to issue discussion 2 on page 46.

Nonylphenol polyethoxylate has been linked to estrogenic effects in wildlife, including fish and amphibians. For a comprehensive look at the nonylphenol ethoxylate surfactants, refer to USDA, 2003.

Poloxalene is of low toxicity on an acute oral basis, with an LD50 value in rats, mice and rabbits exceeding 3 g/kg (III). It is used as an oral veterinary treatment in cattle to cure legume bloat or as a feeding supplement to prevent bloat. It could be used here as an anti-foam agent or as a nonionic surfactant.

Polyoxypropylene oleate butyl ether (CAS 37281-78-0) is probably a minor component of Dyne-Amic®, likely used as an antifoam agent. It is a product recognized by the US Food and Drug Administration as being generally safe when used as an antifoam agent in food packaging (21 CFR 176.200).

Dyne-Amic® contains ethoxylated ingredients. Ethoxylates are formed by reactions of ethylene oxide. In the manufacturing process, some unreacted ethylene oxide as well as the contaminant 1,4-dioxane can become part of the final formulation. Both of these chemicals are considered likely human carcinogens. For a comprehensive look at the risks of 1,4-dioxane in the POEA surfactant, refer to Borrecco and Neisess 1991. For a comprehensive look at the risks of ethylene oxide in ethoxylated surfactants, refer to USDA, 2003.

Crop Oils and Crop Oil Concentrates

Kerosene

Kerosene is included in Garlon 4 formulations of triclopyr. It is on EPA list 3. For a comprehensive look at kerosene, refer to SERA 2003b and USDA 1992.

Agri-dex® (Helena Chemical Co.) and Red-Top Mor-Act® Adjuvant (Wilbur-Ellis Co.)

Agri-dex® and Red-Top Mor-Act® both have a Caution signal word. They may be mildly irritating to the skin and eyes.

Although both materials are from different manufacturers, the identified ingredients are generically similar to discuss together.

The primary ingredient in both products is a paraffin base oil. The paraffin base petroleum oil assigned the CAS numbers in Agri-dex® (83% of the formulation) is described as a solvent refined paraffinic distillate containing a mixture of hydrocarbons having carbon numbers predominantly in the range C20-C50 (heavy paraffinic) or C15-30 (light paraffinic). The light paraffin oil is also identified as a horticultural spray oil. It is of low oral and dermal acute toxicity. The paraffin oil mixtures are not on the U.S. EPA inerts list, although other paraffinic oils are on List 2 and List 3. The oil mixture in Red-Top Mor-Act® (83% of formulation) is on U.S. EPA list 3. It is also referred to as mineral oil, with low acute oral toxicity (LD_{50} of 24 g/kg). This oil is also used in many personal care products such as baby oil and cosmetics. The reason why certain paraffinic oils are on the U.S. EPA inerts list and others are not is not apparent (SERA 1997a).

The name polyol fatty acid ester refers to unspecified fatty acid esters of unspecified alcohols. Similarly, the name polyethoxylated polyol fatty acid ester refers to a group of chemicals that consist of unspecified fatty acid esters of unspecified polyethoxylated alcohols (SERA 1997a). Without further identity, no definitive statements can be made concerning the toxicity of these compounds.

Agri-dex® and Red-Top Mor-Act® contain ethoxylated ingredients. Ethoxylates are formed by reactions of ethylene oxide. In the manufacturing process, some unreacted ethylene oxide as well as the contaminant 1,4-dioxane can become part of the final formulation. Both of these chemicals are considered likely human carcinogens. For a comprehensive look at the risks of 1,4-dioxane in the POEA surfactant, refer to Borrecco and Neisess 1991. For a comprehensive look at the risks of ethylene oxide in ethoxylated surfactants, refer to USDA, 2003.

<u>Herbimax® Petroleum Oil-Surfactant Adjuvant</u> (Loveland Products, Inc.)

Herbimax® has a Caution signal word. This product may be mildly irritating to the skin and moderately irritating to the eyes.

The primary ingredient in Herbimax® is a light paraffin base oil and a oil-based solvent. The paraffin base petroleum oil assigned the CAS numbers in Herbimax® is described as a light paraffinic petroleum distillate. It is of moderate to low toxicity (acute oral $LD_{50} > 5$ g/kg, dermal $LD_{50} > 2$ g/kg). The oil-based solvent is also referred to as light aliphatic solvent naphtha. High levels of acute naphtha exposure can result in central nervous system depression; studies have shown that chronic exposures are no more hazardous than the acute exposures. Naphtha is a flammable material. Both the paraffin oil and the naphtha solvent are on EPA List 2 of potentially toxic inert ingredients.

The label and MSDS identify an alkylphenol ethoxylate as a minor component. This is likely to be a nonylphenol ethoxylate. Nonylphenol polyethoxylate has been linked to estrogenic effects in wildlife, including fish and amphibians. For a comprehensive look at the nonylphenol ethoxylate surfactants, refer to USDA, 2003.

The label and MSDS also identify tall oil fatty acid as a minor component. Tall oil fatty acid is a mixture of oleic, linoleic, and rosin acids derived from the hydrolysis of tall oil, a byproduct of wood pulp. Tall oil fatty acid is included in various cosmetics, such as hair dyes and bleaches,

shampoos, skin cleansing preparations, and a shaving cream. Tall oil fatty acid is approved for use as an indirect food additive. When fed to rats as 15% of the total caloric intake, tall oil fatty acid was nontoxic; however, it had a growth-retarding effect. No treatment-related effects were observed in rats fed diets containing 5% and 10% tall oil fatty acid over two generations. Liquid soap formulations containing up to 12% tall oil fatty acid did not cause dermal irritation, sensitization, or photosensitization in human subjects. One study in rats indicated that this compound had little effect on reproduction. For further information, refer to Anonymous (1989).

Herbimax® contains ethoxylated ingredients. Ethoxylates are formed by reactions of ethylene oxide. In the manufacturing process, some unreacted ethylene oxide as well as the contaminant 1,4-dioxane can become part of the final formulation. Both of these chemicals are considered likely human carcinogens. For a comprehensive look at the risks of 1,4-dioxane in the POEA surfactant, refer to Borrecco and Neisess 1991. For a comprehensive look at the risks of ethylene oxide in ethoxylated surfactants, refer to USDA, 2003.

Fertilizer/Surfactant Mixtures

First Choice® Exciter Activator – Penetrant (Western Farm Service, Inc.)
Magnify Activator – Penetrant (Monterey AgResources)
Class Act® Next Generation (Agrilliance, LLC)
Intensify Activator/Penetrant (West Link Ag)

All four of these products are sufficiently similar so that they can be discussed together. All four have a Caution signal word. They are considered mildly irritating to the skin and eyes. It is assumed in this review that any toxicity data for the full formulations should be able to be used interchangeably with these four products. Class Act® may be an exception because of the differences with the ammonium compounds.

The wetter/spreader specifically identified in First Choice® is a corn syrup derivative, referred to as alkyl polyglycoside. It is assumed this is the same material used in the other three. This same surfactant product is sold under the trade name of Dow Triton CG-110. According to the MSDS for Dow Triton CG-110, this material is of low acute toxicity (oral LD50 > 5 g/kg, dermal LD50 >5 g/kg), although it is an eye irritant. It is used as a detergent and wetter/spreader in personal care products such as shampoo and skin cream because of its mild skin effects. It is of low aquatic toxicity, with a 48-hour NOEC for Daphnia of 150 mg/L and a 96-hour NOEC for fathead minnow of 125 mg/L.

The Class Act® label specifically identifies corn syrup as a component of the product. The other products list unidentified oligosaccharides, which could be corn syrup, or some other mix of simple sugars. It is unclear of the purpose of these sugars although these are listed as part of the surfactant mixture. Corn syrup is a common ingredient in foods.

The sources of nitrogen in these products are ammonium sulfate (in all four) and ammonium nitrate (found in all but Class Act®). Both chemicals are on EPA List 4B. Both are commonly used fertilizers in commercial garden products.

Ammonium sulfate is a water soluble compound. It is mildly irritating to the skin and eyes. It is of low oral toxicity, with a mouse LD_{50} of 640 mg/kg (III). In limited testing ammonium sulfate

has not been shown to be a mutagen or carcinogen. It is of low aquatic toxicity, with a rainbow trout 96-hour LC_{50} of 173 mg/L, a 96-hour EC_{50} for Daphnia of >100 mg/L, and an 18-day EC_{50} for green algae of 2,700 mg/L. A recent study with three amphibian species showed that ammonium sulfate was more toxic to amphibians than the tested fish, with a 10-day NOEAC of 17 to 83 mg/L ammonium-nitrogen equivalent for the amphibians and 67 to 134 mg/L for fathead minnow (Nebeker and Schuytema 2000).

Ammonium nitrate is also a water soluble compound. In its dilute form as found in these products, it is mildly irritating to the eyes and skin; in its concentrated form, it can cause chemical burns. Ammonium nitrate has gained some notoriety as a component of low cost but dangerous explosive mixtures. It is of low acute toxicity , with an oral (rat) LD_{50} of >2 g/kg (III) and a dermal LD_{50} (rabbit) of >5 g/kg (III). Hazards of oral ingestion include interference with the oxygen carrying capacity of the blood., respiratory irritation, and low blood pressure. It has not been demonstrated as a carcinogen, mutagen, or teratogen. The dilute solution (20%) is of low aquatic toxicity with a fish (Chinook salmon, rainbow trout, bluegill) 96-hour LC_{50} of 420-1,360 mg ammonium-nitrogen equivalent/L. The Daphnia EC_{50} is 555 mg/L. It can encourage algae growth, which may affect water quality. A recent study with red-legged frog embryos and larvae showed that ammonium nitrate was more toxic to this species of frog than the tested fish, with a 16-day LC_{50} of 72 mg/L and a 16-day NOEAC of 6.4 mg/L ammonium-nitrogen equivalent (Schuytema and Nebeker 1999).

The large percentage of inert ingredients (about 49%) in these products is troublesome. It is unknown if this is all or mostly water or made up of other ingredients.

Acidifiers

LI-700® (Loveland Products, Inc.)

LI-700® has a Danger signal word, because of its corrosiveness (toxicity category 1 for both dermal and ocular effects) that is primarily due to the presence of methylacetic acid, also referred to as propionic acid. LI-700® is not exceptionally acutely toxic orally, dermally, or via inhalation. It is commonly used as an acidifier in pesticide mixtures.

The name phosphatidylcholine refers to a group of chemicals that consist of unspecified fatty acid diglycerides linked to the choline ester of phosphoric acid. This group includes the naturally occurring lecithins, which are prominent phospholipids in biological cell membranes. Soya lecithins are used as emulsifiers in a wide variety of food products. (SERA 1997a)

The nonionic surfactant contained in LI-700® is identified as alkyl polyoxyethylene ether, which is likely an ethoxylated linear alcohol; however its exact composition is not specified. Several of the articles discussed in the issue questions at the end of this paper concern ethoxylated alcohols.

LI-700® may contain ethoxylated ingredients. Ethoxylates are formed by reactions of ethylene oxide. In the manufacturing process, some unreacted ethylene oxide as well as the contaminant 1,4-dioxane can become part of the final formulation. Both of these chemicals are considered likely human carcinogens. For a comprehensive look at the risks of 1,4-dioxane in the POEA surfactant, refer to Borrecco and Neisess 1991. For a comprehensive look at the risks of ethylene oxide in ethoxylated surfactants, refer to USDA, 2003.

Tri-Fol Acidifier and Buffering Agent (Wilbur-Ellis Co.)

Tri-Fol has a Caution signal word. It is an eye irritant and a mild skin irritant.

The acidifier in Tri-Fol is citric acid (25% of the formulation). Citric acid is of low oral toxicity (mouse LD50 > 3 g/kg (III)). Citric acid is used in many personal care products and is found in foods, although not to the concentration found in Tri-Fol. Citric acid in concentrated form can be severely irritating to the eyes and can cause skin sensitization.

Calcium chloride is of low oral toxicity (LD_{50} 0.9 to 2.1 g/kg (III)). In concentrated liquid forms, it can be very irritating to the skin and eyes, and in its solid form if swallowed can react with water in an exothermic reaction that can cause burns. As a solid, it is not particularly toxic dermally (LD_{50} >5 g/kg, III). It is of low aquatic toxicity with an LC_{50} in bluegill of 8,350 – 10.650 mg/L and an LC_{50} of 759 mg/L with Daphnia. It is used in small amounts in some foods as a substitute for salt, or as part of electrolyte drinks. It is used as a de-icer for roads.

The large percentage of inert ingredients (66%) in this product is troublesome. It is unknown if this is all or mostly water or made up of other ingredients.

Drift Reduction Agents

In-Place® Deposition and Drift Management Agent (Wilbur-Ellis Co.)

In-Place® has a Caution signal word. It is an eye irritant, and a mild skin irritant. None of the ingredients are sufficiently identified on the label or MSDS to characterize their risk. In older communications with the company, the Forest Service was told that the amine salts of organic acids were on EPA List 3 and were slight skin and eye irritants. The Forest Service was told that the aromatic acid is on EPA List 4 and is on the FDA's list of materials generally recognized as safe.

Recently, the company has informed the Forest Service that the petroleum distillate (Stoddard solvent which is on EPA's List 2) has been replaced by a combination of a modified seed oil and a mineral oil. Both have been identified as being on EPA List 3. Neither is identified sufficiently to characterize their risk.

Sinker Polymer Carrier and Drift Retardant (Helena Chemical Co.)

Sinker has a Caution signal word. It is a mild skin and eye irritant. The principal active ingredient cannot be identified exactly from the label or MSDS, however it might be polyacrylamide, which is of low oral toxicity and is used in many personal care products. While the label calls the active ingredient polyacrylamide, the MSDS calls the ingredient a blend of polyacrylamide polymers, so this characterization may not be accurate.

The large percentage of inert ingredients (70%) in this product is troublesome. It is unknown if this is all or mostly water or made up of other ingredients.

Defoamers

Foaminator™ Dry Antifoaming/Defoaming agent (Agrilliance, LLC)

Foaminator™ has a Warning signal word. It is an eye irritant; the label calls for protective eyewear when handling. The label states that the material is harmful if swallowed, although no acute toxicity figures are available.

Compounded silicone (polydimethylsiloxane) is on EPA list 4B. The compounded silicone is practically non-toxic on an acute oral basis (rat LD_{50} >17 g/kg).

Polypropylene glycol (PPG) is a generic name for a large class of polymers. The exact size of the polypropylene glycol in Foaminator™ is not specified. PPG is commonly used in personal care products such as shampoo. PPG is of low acute toxicity, with oral LD_{50} values from 2 to >15 g/kg (III-IV) and acute dermal LD_{50} values >10 g/kg (III).

Silicon dioxide is identified as part of the active ingredients in Foaminator™, although it is more commonly used as an inert carrier. It does have some insecticidal properties, but this is through physical abrasion of protective oils, causing desiccation rather than through direct insect toxicity. It is of low acute toxicity, with an oral LD50 value of 3 g/kg (III). Silicon dioxide is a processed food additive (an anticaking agent) allowed by US FDA (21 CFR 172.480).

The large percentage of inert ingredients (84.5%) in this product is troublesome. As this is a dry formulation, this inert fraction is not water.

No Foam Defoamer (Wilbur-Ellis Co.)
No Foam Dry Defoamer (Wilbur-Ellis Co.)

These two products contain the same active ingredients so can be discussed together. Both have a Caution signal word. Both are moderate eye irritants

The formulation of compounded silicone (polydimethylsiloxane) found in these two products is on EPA list 4B. The compounded silicone is practically non-toxic on an acute oral basis (rat LD_{50} >17 g/kg). On the No Foam label, this is identified as "food grade" active silicone.

The large percentage of inert ingredients (90%) in these products is troublesome. As No Foam Dry is a dry formulation, this inert fraction is not water. It is identified on the label as an inorganic/organic carrier. The inert in No Foam may be water.

No Foam® B (Creative Marketing & Research, Inc.)

No Foam® B has a Caution signal word. No Foam® B is mildly irritating to the skin and eyes; the label requires waterproof gloves when handling. It is of low oral toxicity, with an LD_{50} value of >5 g/kg (IV).

The primary active ingredient in No Foam® B is the nonionic surfactant nonylphenol polyethoxylate. The older sample labels available on-line identify this as an octylphenol polyethoxylate, whereas the newer MSDS identifies it as nonylphenol polyethoxylate. Nonylphenol polyethoxylate has been linked to estrogenic effects in wildlife, including aquatic

species, such as fish and amphibians. For a comprehensive look at the nonylphenol ethoxylate surfactants, refer to the USDA, 2003.

No Foam® B contains dodecylbenzene sulfonate, otherwise known as dodecylbenzene sulfonic acid. Dodecylbenzene sulfonic acid is probably the compound meant to serve as a buffer in this product. It is of low oral toxicity, with an LD_{50} value of 650 mg/kg (III). In its concentrated form, being an acid, it is extremely irritating to the eyes and skin, as well as the respiratory tract.

There is an anionic surfactant, ethanolamine, that is identified on the No Foam® B label. It is of low acute oral toxicity with oral LD_{50} values ranging from 620 to 1720 mg/kg (III) and is moderately toxic dermally with an LD_{50} value of 1 g/kg (II). It is commonly used as an ingredient in personal care products, such as hand lotions and hair care products. In its concentrated form it is a strong eye and skin irritant, and is moderately basic (pH of 10). Based on chronic tests, ethanolamine may be a reproductive and developmental toxicant.

Isopropyl alcohol is considered of low toxicity (acute oral LD_{50} of 5 g/kg in rat), however it is about twice as toxic as ethanol (the alcohol found in alcoholic beverages).

Sodium xylene sulfonate is included in No Foam® B as a minor component, probably to help the various ingredients stay dissolved in water. It is of low acute toxicity, with an oral LD_{50} of >5 g/kg (IV). It is of low aquatic toxicity with minnow and Daphnia acute NOECs of 1,000 mg/L.

No Foam® B contains ethoxylated ingredients. Ethoxylates are formed by reactions of ethylene oxide. In the manufacturing process, some unreacted ethylene oxide as well as the contaminant 1,4-dioxane can become part of the final formulation. Both of these chemicals are considered likely human carcinogens. For a comprehensive look at the risks of 1,4-dioxane in the POEA surfactant, refer to Borrecco and Neisess 1991. For a comprehensive look at the risks of ethylene oxide in ethoxylated surfactants, refer to USDA, 2003.

The large percentage of inert ingredients (75%) in this product is troublesome. It is unknown if this is all or mostly water or made up of other ingredients.

<u>Colorants</u>

<u>Colorfast™ Purple</u>

Colorfast™ Purple dye is not required to be registered, therefore it has no signal word associated with it. It is mildly irritating to the skin, but because of the acetic acid content, can be severely irritating to the eyes, and can cause permanent damage. The label requires the use of acid-resistant gloves and goggles to prevent unnecessary exposures. It would likely be considered a Category 1 material and have a Danger signal word if it carried one.

Acetic acid is the ingredient in household vinegar, although vinegars are normally 4-10% acetic acid, whereas Colorfast™ Purple contains 23.4% by weight. Acetic acid is a very strong eye and skin irritant, and eye exposure can be very hazardous, with permanent damage a possibility.

Gentian Violet is the dye component of Colorfast™ Purple. Gentian Violet is used as an antifungal or antibacterial medication for dermal or mucous membrane infections. Gentian

Violet is a suspected carcinogen, based on tests in mice. It is of moderate acute toxicity, with a LD_{50} value of 96 mg/kg (II).

For a comprehensive look at Colorfast™ Purple dye, including a risk assessment of the suspected carcinogen Gentian Violet, refer to SERA 1997b.

Dipropylene glycol is of low acute and chronic toxicity. It is found in many personal care products. It is minor skin and eye irritant. It is not a carcinogen or a teratogen. The acute oral LD_{50} is 10.6 g/kg (IV) and the acute dermal LD_{50} is 20.5 g/kg (IV). At high (multi-gram) chronic doses, effects are seen to the kidney and liver. It is of low aquatic toxicity.

Hi-Light® Blue

Hi-Light® Blue dye is not required to be registered as a pesticide; therefore it has no signal word associated with it. It is mildly irritating to the skin and eyes. It would likely be considered a Category III or IV material and have a Caution signal word if it carried one.

Hi-Light® Blue is a water-soluble dye that contains no listed hazardous substances. It is considered to be virtually non-toxic to humans. Its effect on non-target terrestrial and aquatic species is unknown, however its use has not resulted in any known problems. The dye used in Hi-Light® Blue is commonly used in toilet bowl cleaners and as a colorant for lakes and ponds (SERA 1997b).

Table 1 – Standard Mammalian Acute Toxicity Testing Results[7]

Name	Oral LD_{50}	Dermal LD_{50}	Inhalation LC_{50}
Ethoxylated fatty amines			
Entry™ II, POEA	1.2 to 14 g/kg (III)	NA	NA
Alkylphenol ethoxylate-based wetter/spreaders			
R-11®	>3.7 g/kg (NPEO) (III)	>2 g/kg (NPEO) (III)	>25 mg/L (est.) (IV)
Activator 90	3.87 to 5.0 g/kg (III)	>2 g/kg (III)	>1.33 mg/L in males (lowest) (III)
X-77®	3.87 to 5.0 g/kg (III)	>2 g/kg (III)	>1.33 mg/L in males (lowest) (III)
Pro-Spreader Activator	>3.3 g/kg (III)	>2 g/kg (III)	NA
Latron AG-98® (N)	>5 g/kg (NPE) (IV) 0.79 g/kg (butanol) (III)	>3 g/kg (NPE) (III) 3.4 g/kg (butamol) (III)	NA
Latron AG-98®	2 g/kg (III)	3 g/kg (III)	NA
Alcohol ethoxylate-based wetter-spreader			
Activator N.F.	NA	NA	NA
Silicone-based wetter/spreaders			
Sylgard® 309	>2 g/kg (III)	>2 g/kg (III)	NA
Freeway®	>2 g/kg (III)	>2 g/kg (III)	NA
Dyne-Amic®	>5.05 g/kg (IV)	>2.02 g/kg (III)	NA
Silwet L-77®	>2.0 g/kg (III)	>2 g/kg (III)	NA
Kinetic	3.3 g/kg (III)	>2 g/kg (III)	NA
Sticker/Spreaders			
Bond®	>5 g/kg (IV)	>2 g/kg (III)	4.73 mg/L (III)
Tactic™	>5 g/kg (IV)	>2 g/kg (III)	>0.19 mg/L (4 hr)
R-56®	NA	NA	NA
Cohere®	NA	NA	NA
Oils			
MSO®	>5 g/kg (IV)	> 4 mg/kg (III)	NA
Hasten®	>5 g/kg (IV)	>5 g/kg (III)	5.79 ml/L (III)
Improved JLB Oil Plus	>5 g/kg (IV)	>3.16 g/kg (III)	NA
Cide-Kick®	>5 g/kg (IV)	NA	>5.16 mg/L (III)
Cide-Kick® II™	>5 g/kg (IV)	>2 g/kg (III)	>90.04 mg/L (IV)
Cygnet Plus	NA	NA	NA

[7] NA indicates data was not available. Roman numerals in parentheses indicate the corresponding toxicity category (refer to page 41)

Blends of vegetable oils and silicone-based surfactants			
Syl-tac™	>5 g/kg (IV)	>5 g/kg (III)	>2.07 ml/L (III)
Phase™	>5 g/kg (IV)	>2 g/kg (III)	>0.19 mg/L
Crop Oils and Crop Oil Concentrates			
Kerosene	28 g/kg (IV)	>2 g/kg (III)	NA
Agri-dex®	>5.01 g/kg (IV)	>2.02 g/kg (III)	NA
Mor-Act®	>5 g/kg (IV)	NA	NA
Herbimax®	>5 g/kg (IV)	>2 g/kg (III)	NA
Fertilizer/Surfactant Mixtures			
First Choice® Exciter	NA	NA	NA
Magnify	NA	NA	NA
Class Act® Next Generation	NA	NA	NA
Intensify	NA	NA	NA
Acidifiers			
LI-700®	>5 g/kg (IV)	>5 g/kg (III)	>6.04 mg/L (III)
Tri-Fol	NA	NA	NA
Drift Reduction Agents			
In-Place®	NA	NA	NA
Sinker	>9.8 g/kg	>9.8 g/kg	NA
Defoamers			
Foaminator™	NA	NA	NA
No Foam	NA	NA	NA
No Foam Dry	NA	NA	NA
No Foam® B	>5 g/kg (IV)	NA	NA

Table 2 – Standard Acute Aquatic Species Toxicity Testing Results

Name	Rainbow Trout 96-hour LC_{50}	Bluegill 96-hour LC_{50}	Daphnia 48-hour EC_{50}
Ethoxylated fatty amines			
Entry™ II, POEA	4.2 mg/L	1.3 – 2.9 mg/L	2.0 mg/L
Alkylphenol ethoxylate-based wetter/spreaders			
R-11®	3.8 – 6 mg/L NOEC 1 mg/L	4.2 mg/L NOEC 1 mg/L	5.7 - 19 mg/L NOEC (population size) 0.25 mg/L
Activator 90	NA	Guppy (*Poecilia reticulata*?) 12.7 mg/L, NOEC 5.8 mg/L	5.2 mg/L (24 hour) NOEC 1 mg/L
X-77®	NA	5 mg/L; Guppy (*Poecilia reticulata*?) 12.7 mg/L, NOEC 5.8 mg/L	5.2 mg/L (24 hour) 2.0 -16.4 mg/L (48 hour) (zero population growth con'c = 13 mg/L)
Pro-Spreader Activator	3.3 mg/L NOEC < 1.0 mg/L	6.0 mg/L NOEC 1.8 mg/L	7.3 mg/L NOEC 3.2 mg/L
Latron AG-98® (N)	NA	NA	NA
Latron AG-98®	10 mg/l	11 mg/l	21 mg/l
Alcohol ethoxylate-based wetter-spreader			
Activator N.F.	NA	NA	NA
Silicone-based wetter/spreaders			
Sylgard® 309	NA	Fathead minnow >4.6 mg/L	22.9 to >41 mg/L (zero population growth con'c = 18 mg/L)
Freeway®	NA	29.7 mg/L	NA
Dyne-Amic®	NA	26.9 mg/L	NA
Silwet L-77®	NA	Zebrafish 2.75 mg/L NOEC 0.56 mg/L	6.2 – 23.4 mg/L (zero population growth con'c = 28 mg/L) NOEC 10 mg/L
Kinetic	NA	19.8 mg/L	111 mg/L (zero population growth con'c = 25 mg/L)
Sticker/Spreaders			
Bond®	NA	NA	614 mg/L (zero population growth con'c = 450 mg/L)

Tactic™	NA	NA	NA
R-56®	NA	NA	NA
Cohere®	NA	NA	NA
Oils			
MSO®	NA	NA	NA
Hasten®	74 mg/L	NA	>50 mg/L
Improved JLB Oil Plus	NA	NA	NA
Cide-Kick®	11 mg/l	10.2 - 18 mg/l	3.9 mg/l
Cide-Kick® II™	NA	NA	NA
Cygnet Plus	NA	30.2 mg/L	NA
Blends of vegetable oils and silicone-based surfactants			
Syl-tac™	>5 mg/L	NA	>5 mg/L
Phase™	NA	NA	NA
Crop Oils and Crop Oil Concentrates			
Kerosene	NA	NA	NA
Agridex®	271 mg/L	>1000 mg/L	>1000 mg/L
Mor-Act®	NA	NA	NA
Herbimax®	NA	NA	NA
Fertilizer/Surfactant Mixtures			
First Choice® Exciter	NA	NA	NA
Magnify	>100 mg/L NOEC 100 mg/L	NA	7.7 mg/L
Class Act® Next Generation	NA	NA	NA
Intensify	NA	NA	NA
Acidifiers			
LI-700®	17 - 130 mg/L	60.8 - 210 mg/L	170-190 mg/L NOEC 100 mg/L
Tri-Fol	NA	NA	NA
Drift Reduction Agents			
In-Place®	NA	NA	NA
Sinker	NA	NA	NA
Defoamers			
Foaminator™	NA	NA	NA
No Foam	NA	NA	NA
No Foam Dry	NA	NA	NA
No Foam® B	NA	NA	NA

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USDA Forest Service, 2003. Human and ecological risk assessment of nonylphenol polyethoxylate-based (NPE) surfactants in Forest Service herbicide applications. Unpublished Report, written by David Bakke, Pacific Southwest Region Pesticide-Use Specialist. May 2003. 182 pages.

5. Issue Discussions Dealing With Surfactants

1. **Can surfactants cause pesticides to move more readily in the soil, or resolubilize, hence causing an increased risk of pesticide movement offsite into water? Can they cause effects to soil systems so that environmental decomposition of pesticides is affected?**

Based on the following studies, it appears that the ability to increase the mobility of other materials throughout the soil profile is a function of the concentration of the surfactant in the soil solution. Surfactants have been used as tools for site amelioration of soil pollution, through their ability to solubilize hydrophobic compounds.

Surfactants applied to the soil, as part of a pesticide application, or in subsequent applications, would remain on the soil surface until decomposed unless driven down by water, thereby also diluting the surfactant in the soil/water system. Based on the studies that follow, for desorption to occur, concentrations of surfactants must be high, in the range of 1,000 ppm or more. This level is unlikely to be reached in normal applications. As an example, if a surfactant were at 2.5% dilution in an herbicide mixture applied at 40 gallons per acre, it would be applied to the soil at a rate of 0.0935 mg/cm^2 (assuming 100% application to the soil, and no foliar or litter interception):

$$\frac{40\ \text{gal}}{\text{ac}} \times .025 \times \frac{1\ \text{ac}}{43560\ \text{ft}^2} \times \frac{3.785\ \text{L}}{\text{gallon}} \times \frac{1000\ \text{cm}^3}{\text{Liter}} \times \frac{1\ \text{g}}{\text{cm}^3} \times \frac{1\ \text{ft}^2}{929\ \text{cm}^2} = 0.0935\ \text{mg/cm}^2$$

If there were about 1 inch of rainfall (2.54 cm) to move this material into the soil, the surfactant would be diluted to about 37 ppm:

$$0.0935\ \text{mg/cm}^2 / 2.54\ \text{cm} \times 1000\ \text{cm}^3/\text{L} = 36.8\ \text{mg/L (ppm)}$$

It appears that biodegradation of pesticides can be affected by surfactants in the soil, however this too is concentration dependent similar to desorption effects. It appears that effects to pesticide biodegradation are through preferential degradation of the surfactant rather than through a toxic action on microorganisms.

Both of these effects (desorption and mineralization of pesticides) are related to the critical micelle concentration (CMC) of the surfactant. The CMC is the point of concentration of a surfactant at which increasing the concentration no longer decreases the surface tension of the surfactant mixture. At this point, increasing surfactant concentrations result in the formation of micelles, or grouped formations of molecules. These micelles can act to attract hydrophobic compounds like oils, which are attracted to the hydrophobic cores of the micelles. This is basically the reason that soaps can clean skin or fabric of oil-based stains. CMC values can vary substantially depending upon the matrix the surfactant is in, such as water or a soil/water mixture. CMC values in water are generally much lower than the corresponding CMC levels in a soil/water matrix, hence the need for very high levels of surfactants in soils prior to solubilization of hydrophobic compounds.

Although the potential exists for surfactants to affect the environmental fate of herbicides in soil, any potential effects would be unlikely under normal conditions because of the relatively low concentration of surfactants in the soil/water matrix. Localized effects could be seen if a spill occurred on soil, so that concentrations of surfactant approached or exceeded about 1,000 ppm.

References:

Abu-Zrieg, M., R. Rudra, W. Dickinson. 2000. Influence of surfactants on leaching of atrazine through soil columns. *Toxicological and Environmental Chemistry.* Vol. 75:1-16.

This study involves the application of two non-ionic surfactants (Rexol 25/7 and Rexonic N25-7, not further identified) and one anionic surfactant (Sulphonic Acid LS, not further identified) to soil columns with subsequent measurement of movement of atrazine. This study used approximately 3-inch soil columns, saturated with surfactant at 200, 1000, 3000 mg/L. Sulphonic Acid LS decreased atrazine movement. The two non-ionic surfactants increased movement of atrazine except for lower dose of Rexonic in a loam soil.

Beigel, C., E. Barriuso, R. Calvet. 1998. Sorption of low levels of nonionic and anionic surfactants on soil: effects on sorption of triticonazole fungicide. *Pesticide Science.* 54:52-60.

Low levels (<1000 mg/L or ppm) of nonionic NPE-based surfactants caused little or no decrease in sorption of a fungicide. At 10,000 mg/L, an increase in sorption was seen. The authors state that reported desorption of contaminants are a result of exceptionally high surfactant application rates (one study referenced here used 100,000-200,000 mg/L). Increase in sorption postulated two ways: 1) an increase in soil organic carbon content as a result of surfactant addition created increased affinity for bonding: 2) at low levels, the surfactant sorbs to soil through hydrophobic interactions, leaving the hydrophilic heads to extend into soil solution, increasing desorption. As more surfactant is added, a bilayer of surfactant is created on soil, with hydrophobic tails of second layer sticking into solution, creating an affinity for additional sorption.

Bramwell, D.P., S. Laha. 2000. Effects of surfactant addition on the biomineralization and microbial toxicity of phenanthrene. *Biodegradation.* 11(4):pp 263-277.

This study looks at biomineralization and toxic effects of the PAH phenanthrene as affected by the presence of four surfactants in aqueous and soil-water systems. The four surfactants are the nonionic surfactant Tween 20 (polyoxyethylene sorbitan monolaurate); sodium dodecyl sulfonate (SDS), an anioic surfactant; TTAB, a cationic surfactant; and Citrikleen (a commercial emulsifier). High doses of Tween 20 applied to soil are needed to inhibit mineralization of phenanthrene (=>5000 mg/L). Doses above 5,000 mg/L of Tween 20, TTAB, and Citrikleen, and doses above 8,000 mg/L of SDS are needed to solubilize phenanthrene in soil-water systems. It may be that mineralization is affected due to preferential mineralization of the surfactant.

Authors report on another study where Triton X-100 (an octylphenol polyethoxylate, with 9-10 ethoxylates) at 12 mg/L neither enhanced nor inhibited the biodegradation rate of naphthalene by bacteria, whereas a concentration of 12,000 mg/L enhanced biodegradation

(Milhelcic et al 1995). Other studies show inhibitory or improvement of degradation of PAHs.

Garcia, J.M., L.Y. Wick, H. Harms. 2001. Influence of the nonionic surfactant Brij 35 on the bioavailability of solid and sorbed dibenzofuran. *Environ. Sci. Technol.* 35:2033-2039.

Used a nonionic linear alcohol ethoxylate surfactant. CMC in water determined as >0.17 g/L (>170 ppm). To elicit solubilization of the test material, density of surfactant had to be greater than CMC. Test then used 10X the CMC (1700 ppm). Consistent with other studies showing need to utilize high rates of surfactants before movement is seen. At concentrations below the CMC, this surfactant had no effect on the dissolution kinetics, indicating that surfactant micelles rather than individual surfactant molecules play a crucial role in dibenzofuran dissolution.

Huggenberger, F., J. Letey, W.J.Farmer. 1973. Effect of two nonionic surfactants on adsorption and mobility of selected pesticides in a soil system. In, *Proceedings, Soil Science Society of America, Volume 37, 1973*. pages 215-219.

Two surfactants (alkylpolyoxyethylene ethanol, a linear alcohol ethoxylate (Soil Penetrant 3685) and a mixture of a polyoxyethylene ester and a polyoxyethylene ether (Aqua Gro)) were applied to soil to test movement of lindane, diuron, and atrazine. Low rates (~50 ppm) had no effect on sorption or mobility; moderate rates (500-2,000 ppm) resulted in an increase in sorption (i.e., less movement), high rates (2,000-10,000 ppm) increased mobility with lindane and diuron. There were no effects to atrazine at any dose.

It is important to remember that surfactants applied to the soil as part of a pesticide application would remain on the soil surface unless driven down by water. This would have the effect of greatly diluting the surfactant in the soil/water system. Hence these authors conclude that at the high dilution rates commonly used for surfactants (~1%) when applied to soil would not result in risk of desorption of pesticides.

Laha, S., R.G. Luthy. 1991. Inhibition of phenanthrene mineralization by nonionic surfactants in soil-water systems. *Environmental Science and Technology*. 25(11):1920-1930.

In the presence of surfactants (alcohol ethoxylate (C12AE4), OP9.5E, and NP10.5E) at concentrations above 0.1% in soil water system (>1,000 ppm), phenanthrene is solubilized. At rates below 0.1%, solubilization was not significantly different than simple aqueous solubility. Rates of surfactants that resulted in micelle formulation in soil/water system completely inhibited the mineralization of phenanthrene. The inhibition was reversible when the surfactant solutions were diluted below the CMC.

Laha, S., R.G. Luthy. 1992. Effects of nonionic surfactants on the solubilization and mineralization of phenanthrene in soil-water systems. *Biotechnology and Bioengineering*. 40(11):1367-1380.

In the presence of surfactants (four linear alcohol ethoxylates (C12AE4, C12AE23, C12-15AE3, C12-15AE4), OP9.5E, NP10.5E, polysorbate 20 and 80, and two high CMC surfactants (CHAPS, and octylglucoside)) at concentrations that resulted in micelle

formulation, solubilization of phenanthrene commenced. Surfactants didn't increase rate of mineralization. Authors also established CMC in soil-water systems for these surfactants (only reported the following: 850 ppm for C12AE4; 560 ppm for OP9.5E). Results supported findings of earlier study (Laha & Luthy 1991) with these additional surfactants.

Mata-Sandoval, J.C., J. Karns, A. Torrents. 2001. Influence of rhamnolipids and Triton X-100 on the biodegradation of three pesticides in aqueous phase and soil slurries. *Journal of Agriculture and Food Chemistry*. 49:3296-3303.

Looked at the effects of adding a surfactant to soils contaminated with trifluralin, atrazine, or coumaphos, focusing on the degradation of these pesticides. Shows the inhibitory effects of nonionic Triton X-100 surfactant (an octylphenol ethoxylate with 9-10 ethoxylate units) on atrazine and coumaphos degradation at high concentrations (2,000 and 4,000 mg/L) in aqueous suspensions in soil. Effect appears dose-dependent, with lower doses (100, 500 mg/L) showing no inhibitory effect. Decrease in degradation assumed to be the result of preferential degradation of surfactant utilizing resources, rather than any toxic effect. Triton X-100 had a positive effect on degradation of trifluralin. Authors state that previous studies have shown that Triton X-100 can sorb to soils, increasing their hydrophobicity, and enhance sorption of pesticides, which means "solubilization of the pesticides may be promoted only at very high surfactant concentrations".

Sanchez-Camazano, M., M. Arienzo, M.J. Sanchez-Martin, T. Crisanto. 1995. Effect of different surfactants on the mobility of selected non-ionic pesticides in soil. *Chemosphere*. Vol. 31, No. 8:3793-3801.

Three surfactants (cationic (TDTMA); anionic (lauryl sulphate); and non-ionic (tween 80, a polyoxyethylene sorbitan monooleate)) were either added to soil prior to adding four pesticides (diazinon, atrazine, metolachlor, acephate), or used as a rinse on soil already contaminated with these same pesticides to see how these pesticides would react (increase or decrease mobility). Application rates ranged from critical micelle concentration (CMC) to 50 g/kg (50,000 ppm) in the application test, and at 5 and 50 g/L (5,000 and 50,000 ppm) in the rinse test.

The cationic surfactant, when added to the soil, decreased the mobility of all 4 pesticides at 0.1, 5 and 50 g/kg. The anionic surfactant, when added to the soil, increased sorption of all four pesticides at 2.38 g/kg, but caused the mobility of diazinon and atrazine to increase at 5 g/kg, and metolachlor to increase at 50 g/kg. Tween 80 added to soil decreased mobility of hydrophobic pesticides (diazinon, atrazine) at levels up to 50 g/kg, but increased the mobility of metolachlor at 5 g/kg (but not at 0.04 g/kg).

The cationic surfactant applied as a rinse had little or no effect at 5 g/L, while at 50 g/L metolachlor sorption was decreased. The anionic surfactant and Tween 80 added in high concentrations (50g/L) as a rinse, increased mobility of these pesticides, while at 5 g/L both had little or no effect.

Sanchez-Camazano, M., M.J. Sanchez-Martin, M.S. Rodriguez-Cruz. 2000. Sodium dodecyl sulphate-enhanced desorption of atrazine: Effect of surfactant concentration and of organic matter content of soils. *Chemosphere*. 41:1301-1305.

Anionic surfactant (sodium dodecyl sulphate) showed increasing desorption of atrazine with increasing soil organic matter and increasing concentration of surfactant. Tested rates are fairly high (1.7 to 23.8 g/L (1,700 to 23,800 ppm) of surfactant) and reflect rates above the critical micellular concentration (except for lowest rates, at 0.75 of CMC). Results show desorption of atrazine greatly increases above the CMC, owing to the affinity of atrazine, as a hydrophobic compound, for the hydrophobic cores of the surfactant micelles. Soils with low organic matter cause sorption to increase at concentrations below the CMC.

Tiehm, A. et al. 1997. Surfactant-enhanced mobilization and biodegradation of polycyclic aromatic hydrocarbons in manufactured gas plant soil. *Environmental Science and Technology*. 31(9):2570-2576.

Two surfactants (an NP30E, Arkopal N-300; and a 12-carbon alkylpenol with 30 ethoxylate groups, Sapogenat T-300) enhanced the mass transfer rate of sorbed PAHs into the aqueous phase due to solubilization when added to soil above the CMC. These solubilized PAHs were then available for biodegradation. The rapid degradation of the NP30EO caused a lack of oxygen in soil, resulting in a decrease in biodegradation of the PAHs, however the slower degradation of the 12-carbon surfactant resulted in an increased rate of PAH biodegradation as compared to a mineral medium alone.

2. Do surfactants represent a unique risk to terrestrial or aquatic invertebrates?

Based on a review of the current research, it would appear that surfactants have the potential to affect terrestrial insects. However, as is true with many toxicity issues, it would appear that any effect is dose related. The research does indicate that the silicone-based surfactants, because of their very effective spreading ability, may represent a risk of lethality through the physical effect of drowning, rather than through any toxicological effects. Silicone surfactants are typically used at relatively low rates and are not applied at high spray volumes because they are very effective surfactants. Hence it is unlikely that insects would be exposed to rates of application that could cause the effects noted in these studies. Other surfactants, which are less effective at reducing surface tension, can also cause the drowning effect. But as with the silicones, exposures have to be high, to the point of being unrealistically high, for such effects.

When considering the need for relatively high doses for a lethal effect, combined with the fact that individuals, not colonies or nests of invertebrates, may be affected, there is little chance that the surfactants could cause widespread effects to terrestrial invertebrates under normal operating conditions. Spills or accidents could result in concentrations sufficiently high to cause effects, depending upon the surfactant.

References:

Cowles, R.S., et al. 2000. “Inert” formulation ingredients with activity: Toxicity of trisiloxane surfactant solutions to twospotted spider mites (Acari:Tetranychidae). *Journal of Economic Entomology*. 93(2):180-188.

Testing of Silwet L-77 and several other organosilicone surfactants as miticides. Mites were exposed by dipping leaf surface for 3 seconds into solutions of 0, 4, 9, 20, 45, and 100 ppm of Silwet L-77; results of LC_{50} of 8.61 ppm; LC_{90} of 55.6 ppm. Two other trisiloxanes had similar results. Leaf species made a difference (higher values for $LC_{50/90}$ on strawberry vs bean leaves). Authors propose that these materials perform like extremely active soaps, permitting interaction of water with insect and mite cuticles at a small fraction of the concentration required for conventional insecticidal soaps. Effects probably caused by drowning by permitting water to infiltrate mites' respiratory apparatus. Authors admit that leaf dip is an exaggeration of likely exposures, and would be expected when using high-volume spray techniques, possibly only with high humidity. Important to note that trisiloxane surfactants would not normally be used with high volume applications as the risk of surface runoff and loss of effect is high.

Donoven, B.J., G.S.Elliott. 2001. Honey bee response to high concentrations of some new spray adjuvants. In *54th Conference Proceedings of the New Zealand Plant Protection Conference.* Accessed on-line at http://www.hortnet.co.nz/publications/nzpps/proceedings/01/01_51.pdf on February 19, 2002. 5 pages.

Tested four adjuvants, including two surfactants (Du-Wett, a silicone-based surfactant at 0.1, 0.25, 0.5% and LI-700 at 0.25, 0.5, 1.0%) and two deposition agents (Bond, a carboxylated latex sticker at 0.125, 0.25, 0.5%, and Bond Xtra, a blend of silicones and latex at 0.2, 0.5, 1.0%) both orally and topically against bees. All concentrations of all adjuvants tested topically and orally were non-toxic to bees at doses well above those used in the field. Topical applications were done by applying 1 µl of test solution to each bee (Du-Wett and Bond up to 0.005 mg/bee; LI-700 and Bond X-tra up to 0.01 mg/bee). Observations were made after 4, 24, and 48 hours.

Goodwin, R.M., H.M. McBrydie. 1999. Effects of surfactants used with fungicides, herbicides, and insecticides on honey bee mortality. Confidential report to the National Beekeeper's Association. Accessed on-line at http://www.nba.org.nz/surfactants.html on February 19, 2002. 16 pages

This study showed toxic effects to honey bees when exposed to some of 11 surfactants tested. These 11 surfactants included two silicone-based surfactants (Pulse and Boost), two APE-based surfactants (Citowett and Multifilm), two petroleum oil-based surfactants (Peptoil and Sunspray) and a tallow-amine surfactant (Ethokem). Exposure involved anesthetizing the bees, placing them in petri dishes, and spraying them as they lay in the dish (mortality may have been caused by drowning). Spray volume rates were high given the concentrations (utilizing low-volume recommended concentrations but applying at high volume rates). Four of tested surfactants were toxic to bees (Citowett, Pulse, Boost, and Ethokem).

Because of the treatment method, this study must be carefully interpreted. The application method does not represent normal spray applications, since avoidance responses would be expected in nature, while anesthetized bees cannot avoid the activity. Also the rates of application for several of these surfactants were very high in relation to expected field application rates (lowest rate of application was the equivalent of approximately 155 gallons per acre; highest was 280 gallons per acre).

Henry, C.J., K.F.Higgins, K.J.Buhl. 1994. Acute toxicity and hazard assessment of Rodeo, X-77 Spreader, and Chem-Trol to aquatic invertebrates. *Environmental Contamination and Toxicology*. 27(3):392-399.

X-77, a nonylphenol ethoxylate surfactant mixed with the Rodeo formulation of glyphosate and applied to wetlands as well as in lab acute tox tests. 48 and 96 hour LC_{50} values for X-77 ranged from 2.0 to 14.1 mg/L for 4 species of aquatic invertebrates. This was about 2 orders of magnitude greater acute toxicity than the Rodeo formulation of glyphosate. Mortality patterns in treated and untreated wetlands were similar, indicating a lack of acute toxicity from application of tank mix. Based on application rates applied, and assuming X-77 would be detected at same rate as applied, margin of safety would indicate no acute risk. Little known about chronic effects to aquatic organisms.

Imai, T., S. Tsuchiya, T.Fujimori. 1995. Aphicidal effect of Silwet L-77, organosilicone nonionic surfactant. *Applied Entomology and Zoology*. 30(2):380-382.

0.1% Silwet L-77 was applied to aphids on leaves until leaves were dripping wet. Silwet by itself did not produce a substantial effect under low humidity conditions, but controlled aphids almost completely under high humidity conditions. Makes the conclusion that the use of silicone surfactants as insecticides would only be effective on aquatic insects and small insects such as aphids, whiteflies and mites. With larger insects it would be difficult to expose them to a large enough dose for suffocation to occur (a criticism of the future Goodwyn and McBrydie study on bees).

Paveglio, F.L., et al. 1996. Use of Rodeo and X-77 spreader to control smooth cordgrass (*Spartina alterniflora*) in a southwestern Washington estuary: I. Environmental fate. *Environmental Toxicology and Chemistry*. Vol. 15, No. 6:961-968.

Aerial application of the Rodeo formulation of glyphosate and X-77 , a nonylphenol ethoxylate surfactant, over tidal wetlands at rate of 4.7 L/ha (2 qts/ac) Rodeo and 0.9 L/ha (1% or 0.1 gallons/ac) X-77 in 93.5 L/ha (10 gallons/acre) total volume. Application occurred at low tide, allowing 5 hours prior to inundation. Deposition was measured and sediment samples were taken, both prior to inundation. Seawater samples with the first high tide (1 cm depth) were taken above the plots. Seawater samples were taken when tide had reached 1 meter in depth after treatment. Spartina samples were taken.

69 to 77% of applied glyphosate was detected in sediment, with AMPA residues at 0.4-0.5% of glyphosate. NPEO was sampled at 65 to 85% of applied in sediment. NPEO concentration declined within 14 days post-treatment, likely from microbial degradation, but then stabilized (likely due to partitioning to sediment (hence unavailable for biodegradation) and lower temperatures). NPEO was detected in seawater at 3 to 16 μg/l. NPEO was not detected in deeper seawater (while glyphosate and AMPA were). NPEO was not detected in spartina. NOTE – includes references to plant absorption studies showing 8%, 44-69%, and 2% absorption of surfactants in three studies.

Purcell, M.F., W.J.Schroeder. 1996. Effect of Silwet L-77 and diazinon on three tephritid fruit flies (Diptera: Tephritidae) and associated endoparasitoids. *Horticultural Entomology*. Vol. 89(6):1566-1570.

Demonstrated toxicity of silicone-based surfactant to fruit flies and fruit fly parasitoids. LC_{50} for puparia exposed to Silwet L-77 ranged from 0.098 to 0.145% AI. At 0.5% AI significant decrease in emergence of parasitoid wasps. Indicates that silicone-based surfactants could be considered as an effective alternative to conventional insecticides in treatment of fruit flies in soil. Other studies referenced discuss effects of Silwet L-77 on aphids and thrips. Hypothesis is that because of its very low surface tension, silicone-based surfactants spread rapidly over the insect's body, infiltrating the tracheal system, and the insect dies by drowning.

Simenstad, C.A., et al. 1996. Use of Rodeo and X-77 spreader to control smooth cordgrass (Spartina alterniflora) in a southwestern Washington estuary: 2. Effects on benthic microflora and invertebrates. *Environmental Toxicology and Chemistry*. Vol. 15, No. 6: 969-978.

This associated study with Paveglio et al 1996 looked at effects on benthic invertebrates and found no differences between control and treated areas 119 days after treatment. The authors could not detect either short- or long-term responses by any component of the mudflat community attributable to the application of Rodeo and X-77, including indirect effects from habitat modifications.

3. Do mixtures of herbicides and surfactants represent a greatly increased risk over the individual compounds alone (i.e. synergism)?

Surfactants, by their very nature, are intended to increase the effect of a pesticide by increasing the amount of pesticide that is in contact with the target (by reducing surface tension). This is not synergism, but more accurately is a reflection of increased dose of the herbicide active ingredient into the plant.

Although there is not much data in the technical literature, the references included in this paper indicate a lack of synergistic effects between surfactants and pesticides.

References:

Abdelghani, A.A., et al. 1997. Toxicity evaluation of single and chemical mixtures of Roundup, Garlon 3A, 2,4-D, and Syndets surfactant to channel catfish (*Ictalurus punctatus*), bluegill sunfish (*Lepomis microchirus*), and crawfish (*Procambarus spp.*). *Environmental Toxicology and Water Quality*. 12:237-243.

This study used an anionic surfactant (an ethoxylated alcohol). 96-hour LC_{50} values (static) were determined for bluegill, crawfish, and catfish for the individual chemicals plus mixtures. Results indicate additive rather than synergistic effects between these chemicals in mixtures. This study also shows that this surfactant is more toxic than the individual formulated herbicides.

Henry, C.J., K.F.Higgins, K.J.Buhl. 1994. Acute toxicity and hazard assessment of Rodeo, X-77 Spreader, and Chem-Trol to aquatic invertebrates. *Environmental Contamination and Toxicology*. 27(3):392-399.

This study looked at the effects of X-77 spreader (a nonylphenol ethoxylate-based surfactant) mixed with Rodeo and Chemtrol (drift reducer) and applied to wetlands as well as in lab acute toxicity tests. Mixtures of the three materials, including binary mixtures, indicated additive effects to lethality as tested against 5 invertebrate wetland species.

Lewis, M.A. 1992. The effects of mixtures and other environmental modifying factors on the toxicities of surfactants to freshwater and marine life. *Water Research*. 26(8):1013-1023.

This review paper looked at 58 reports, most dealing with the anionic surfactant linear alkylbenzene sulfonate. Effects of mixtures and water quality parameters is compound specific; difficult to relate individual studies to untested mixtures. One study that is referenced (Wong 1985) looked at mixtures of the octylphenol ethoxylate surfactant Triton X-100, in combination with several organic compounds (including an unidentified algicide and the herbicide 2,4-D) and two metals, and the effects these combinations had on the growth rate of a freshwater algae. The study showed antagonistic effects of the organic compounds and Triton X-100, while showing synergistic effects with the metals.

Oakes, D.J., J.K. Pollak. 1999. Effects of a herbicide formulation, Tordon 75D, and its individual components on the oxidative functions of mitochondria. *Toxicology*. 136(1):41-52.

Tordon 75D contains two herbicides (2,4-D and picloram), a proprietary surfactant (polyglycol 26-2) as well as several other inert ingredients. The authors examined the effects of the components of Tordon 75D (individually and in various combinations) on rat liver mitochondria. Toxic effects of Tordon 75D were not due to any additive or synergistic actions of a mixture of its active and other components, but rather were caused solely by the proprietary surfactant.

Oakes, D.J., J.K. Pollak. 2000. The in vitro evaluation of the toxicities of three related herbicide formulations containing ester derivatives of 2,4,5-T and 2,4-D using sub-mitochondrial particles. *Toxicology*. 151:1-9.

The authors conclude that it is important to look at formulations. The study looked at combined effects of the two herbicides and diesel fuel, as well as with two surfactants (Alkanate CS, anionic, and Teric N12, a nonionic nonylphenol polyethoxylate). The results of this study support additive toxicities of surfactants with active ingredients as well as between active ingredients, rather than any synergistic effects. The method of exposure in this study is not indicative of effects to the whole body, as it doesn't utilize the body's detoxification abilities.

4. Do surfactants represent a unique risk to aquatic organisms?

For a comprehensive review of the effect of nonylphenol ethoxylate-based surfactants to aquatic organisms, refer to USDA 2003.

There is little information in the scientific literature on effects of seed oils and silicone-based surfactants on aquatic organisms. There is more information on linear alcohol ethoxylates (LAE) and alkylphenol ethoxylates, such as nonylphenol ethoxylates (NPE) and octylphenol ethoxylates (OPE) as these have more commercial uses in soaps and detergents, so environmental studies of water treatment plants have generated more data.

The interest in the NPE and OPE surfactants is largely driven by findings of estrogenic effects in fish and other aquatic organisms. From USDA 2003, based on various studies, it can be said that the threshold for estrogenic effects is generally above the threshold for other effects; hence protective levels of NPE exposure would encompass any concerns for estrogenic effects.

With linear alcohol ethoxylates, it appears that toxicity to aquatic organisms increases in relation to increased carbon chain length, but like the NPE-based surfactants, toxicity decreases with increasing ethoxylate length. It does appear that aquatic plants and most aquatic invertebrates are relatively insensitive to alcohol ethoxylates, although some specific invertebrate taxon may be identified as being more sensitive.

Effects on aquatic organisms are driven by the same dose-response principles as any other group of organisms (i.e., dosage thresholds can be determined for various effects). There are interspecies differences, as well as differences within species depending upon age, however the results of studies on the same surfactants are consistent with each other. It does appear that in general, the surfactants used in forestry can affect aquatic organisms at lower doses than for terrestrial organisms.

References:

Buhl, K. J., N.L. Faerber. 1989. Acute toxicity of selected herbicides and surfactants to larvae of the midge *Chironomus riparius*. *Archives of Environmental Contamination and Toxicology*. 18:530-536.

Testing of Rodeo, Activator NF (linear alcohol ethoxylate), and X-77 (a nonylphenol polyethoxylate) against the midge to determine 24- and 48-hour EC_{50} values (based on lack of movement). Rodeo toxicity tests resulted in 24-hour EC_{50} of 5,900 mg/L and a 48-hour EC_{50} of 5,600 mg/kg. The NOEC value for Rodeo was 3,200 mg/L. For X-77 both the 24- and 48-hour EC_{50} equalled 8.6 mg/L. For Activator NF the 24- hour EC_{50} was 10.1 mg/L while the 48-hour EC_{50} was 8.9 mg/L.

Cardellini, P., L. Ometto. 2001. Teratogenic and toxic effects of alcohol ethoxylate and alcohol ethoxy sulfate surfactants on *Xenopus laevis* embryos and tadpoles. *Ecotoxicology and Environmental Safety*. 48:170-177.

This study involved testing a linear alcohol ethoxylate (C12-14, AE-7) at rates of 0, 1, 2, 4, 4.5, 5, 5.5, 6, and 8 mg/L for 72 hours against the common frog test species *Xenopus laevis*. Tested both stage 8 blastulas and stage 46 embryos. 72-hour LC_{50} for the linear alcohol ethoxylate, for embryos, is 4.59 mg/L (ppm). Effects on heart rate and motility at 4.5 mg/L.

Teratogenic effects were observed at doses near LC_{50}. The authors conclude that the embryonic stage is most susceptible to teratogenic effects, when epithelia and gill cartilage in particular suffer malformations. Oxygen consumption was reduced at 3.5 mg/L, the authors assume this is caused by surfactant toxicity to mitochondria. There was rapid recovery from effects after suspension of exposure, indicating an ability to restore function and structure.

Dorn, P.B., et al. 1996. Assessing the effects of a C14-15 linear alcohol ethoxylate surfactant in stream mesocosms. *Ecotoxicology and Environmental Safety*. 34(2):196-204.

This study involved exposure of organisms in a southeast U.S. stream mesocosm to C14-15AE7 (a linear alcohol ethoxylate) at rates from 80 to 550 ppb. Two 30-day periods of exposure between April and August (330 ppb highest dose in first period; 550 ppb highest dose in second period). No effects on periphyton or vascular plants at highest doses. Macroinvertebrates were relatively insensitive (no significant differences between controls and surfactant in terms of number of taxa or abundance) with the exception of Simuliidae (blackflies) (density, which was affected at 160 ppb (NOEC of 80 ppb). Fathead minnow reproduction was significantly reduced at >280 ppb, and larval survival was reduced at 330 ppb. Growth and mortality of bluegill sunfish were not affected at highest exposure of 330 ppb. Lab testing of bluegill showed 96-hour LC_{50} of 700 ppb, 10 day LC_{50} of 600 ppb. Lab testing of fathead minnow showed 96 hour LC50 of 800 ppb and 10-day LC_{50} of 700 ppb. The authors compared the results of mesocosm study with the scientific literature chronic NOECs for these same fish and found comparable results.

Gardner, S.C, C.E. Grue. 1996. Effects of Rodeo and Garlon 3A on nontarget wetland species in central Washington. *Environmental Toxicology and Chemistry*. Vol. 15, No. 4:441-451.

This study involved the application of Garlon 3A and Rodeo along with LI 700 surfactant to an aquatic weed. Garlon 3A (6% by vol), LI 700 (0.5% by vol) and water applied at rate of 0.54 gpa Garlon 3A (approx 11 gpa mix). Rodeo (1% by vol), LI 700 (0.5% by vol) and water applied at rate of 0.1 gpa Rodeo (approx 10 gpa mix). So in both applications, LI 700 was applied at rate of approximately .05 gpa. Although nothing specifically mentioned about LI 700 monitoring or toxicity in this study, this amount of LI 700 and Garlon 3A or Rodeo did not affect trout, Daphnia, or duckweed survival.

Gillespie, W.B., Jr., J.H. Rodgers, Jr., P.B. Dorn. 1998. Responses of aquatic invertebrates to a linear alcohol ethoxylate surfactant in stream mesocosms. *Ecotoxicology and Environmental Safety*. 41(3):215-221.

This study involved exposure of organisms in a southeast U.S. stream mesocosm to C12-13AE6.5 (a linear alcohol ethoxylate) at rates from 320 to 5,150 ppb. Significant effects were seen to population densities of simulids, copepods, and cladocerans during 30-day exposures. 30-day Lowest Observable Effect Concentration (LOEC) is thus 320 ppb for aquatic invertebrates (No Observable Effect Concentration (NOEC) < 320 ppb). No significant differences in drift at any dose, although trends were seen at highest dose. After 2-week post-treatment period, no differences between control and treatment streams. Compared this study with two previous mesocosm experiments (including Dorn et al 1996, below) and determined that toxicity to linear alcohol ethoxylates is positively correlated with

the carbon chain length. One of the previous studies involved a C9-11AE6 linear alcohol ethoxylate, with a 30-day LOEC of 4,350 ppb (Gillespie et al 1997).

Howe, C.M., M. Berrill, B.D. Pauli, C.C. Helbing, K. Werry, N. Veldhoen. 2004. Toxicity of glyphosate-based pesticides to four North American frog species. *Environmental Toxicology and Chemistry*. 23(8):1928-1938.

Acute and chronic exposure tests to four species in which various formulations of glyphosate, as well as the POEA surfactant were tested. In all cases, POEA was more toxic to all four species than glyphosate formulations. In green frog tadpoles, the 96-hour LC50 was 1.1 mg/L for POEA. The authors determined that POEA was the major contributor to Roundup formulation toxicity in these tests.

Jumel, A., M.A.. Coutellec, J.P. Cravedi, L. Lagadic. 2002. Nonylphenol polyethoxylate adjuvant mitigates the reproductive toxicity of fomesafen on the freshwater snail *Lymnaea stagnalis* in outdoor experimental ponds. *Environmental Toxicology and Chemistry*. 21(9):1876-1888.

An outdoor mesocosm study using an NPE-based surfactant (Agral 90), made up of 91-93% NPE and 7-9% isobutanol. Although this study doesn't deal specifically with aquatic toxicity, it does show that adding Agral 90 to the herbicide fomesafen mitigates the reproductive toxicity of the herbicide to an aquatic snail. The authors assume that the surfactant attached to plants and mesocosm walls, making the herbicide unavailable to the snails.

Kline, E.R., R.A. Figueroa, J.H. Rodgers, Jr., P.Dorn. 1996. Effects of a nonionic surfactant (C14-15 AE-7) on fish survival, growth, and reproduction in the laboratory and in outdoor stream mesocosms. *Environmental Toxicology and Chemistry*. Vol. 15, no. 6:997-1002.

A linear ethoxylated alcohol surfactant was tested for 1-10 days against bluegills and fathead minnows at 0, 50, 150, 500, 1,000, and 2,000 µg/L. 96-hour LC_{50} values were 650 and 770 µg/L. 10-day LC_{50} were 560 and 690 µg/L. Exposure data resulted in a NOEC of 160 µg/L for both species for both survival and swimming ability. In 30-day mesocosm experiments, there were no effects to growth or survival below 330 µg/L. No effects on abundance of zooplankton at any dose.

Lewis, M.A. 1991. Chronic and sublethal toxicities of surfactants to aquatic animals: a review and risk assessment. *Water Research*. Vol. 25, No. 1:101-113.

Useful info here references older studies for NP10EO on sublethal responses (behavioral) (Table 4). In Swedmark et al 1976, swimming activity and avoidance were affected at 2-4 mg/L in cod and mussels. In Swedmark et al 1971, effects to mussels, cockles, and barnacles were seen at 2-5 mg/L; effects to locomotion of a decapod, hermit crab and shore crab were seen at 20-40 mg/L. In Hoglund 1976, avoidance behavior to NP10EO in cod was seen at a much lower concentration (0.002 mg/L).

Several studies dealt with linear alcohol ethoxylates (LAE) and invertebrates, with 21-day NOEC for *Daphnia magna* of 0.24 mg/L, and LOEL levels of 0.17 mg/L (7-day for

Ceriodaphnia dubia with effects on reproduction) to 1.75 mg/L (14-day for a clam species, affecting larval growth and development). One study in fish, showed a 28-day NOEC value of 0.18 to 0.32 mg/L with fathead minnows using LAE surfactants (Maki 1979a).

As for sublethal effects in fish, two studies dealing with nonionic surfactants are mentioned. One (Maki 1979b) showed LOEL values of 0.54 mg/L (C14-15 AE6) and >1.56 mg/L (C12-13 AE) for respiration in bluegills. Another (Sutterlin et al 1971) doesn't describe the exact nature of the tested surfactants but found no effects to Atlantic salmon olfactory responses at doses up to 10 mg/L. Swedmark et al 1976 showed effects to swimming activity in cod with an NPE-based surfactant at levels greater than 1 mg/L.

Lewis, M.A. 1992. The effects of mixtures and other environmental modifying factors on the toxicities of surfactants to freshwater and marine life. *Water Research.* 26(8):1013-1023.

This review paper looked at 58 reports, most dealing with the anionic surfactant linear alkylbenzene sulfonate. Effects of mixtures and water quality parameters is compound specific; difficult to relate individual studies to untested mixtures.

One study involving nonylphenol ethoxylate surfactants and copper exposure to rainbow trout showed an antagonistic effect on 14-day survival (Calamari and Marchetti 1973). Another study of nonylphenol ethoxylate surfactants and cadmium exposure to rainbow trout indicated a lack of synergism on 1-hour metal transfer in gills, but a synergistic effect on gill viability (Part et al 1985). Wong 1985 showed a synergistic effect of an octylphenol ethoxylate surfactant in combination with copper or cadmium on freshwater algae 14-day growth rate, but antagonism with an algicide and the herbicide 2,4-D.

Lizotte, R.E., Jr., et al. 1999. Effects of a homologous series of linear alcohol ethoxylate surfactants on fathead minnow early life stages. *Archives of Environmental Contamination and Toxicology.* 37:536-541.

28-day flow-through testing with fathead minnows, using three linear alcohol ethoxylates (C9-11AE6, C12-13AE6.5, C14-15AE7) at nominal concentrations of 0, 1, 3, 5, 7, 10 mg/L for first two and 0, 0.5, 1, 1.5, 2, 2.5 mg/L for the last. 48-hour exposures at any tested dose had no effect on embryo survival. 48-hour NOEC (survival) were 10.27, 8.06, and 2.19 mg/L respectively (highest dose tested). 28-day LC_{50} values were 4.87, 2.39, and 1.02 ppm respectively. Corresponding NOECs for survival were 1.01, 1.76, and 0.74 ppm. 28-day survival decreased with increasing alkyl chain length (carbon chain); polyethoxylate chain length, although not specifically considered, appeared to have no effect. The authors compared their results with previously established data from 96-hour, 10-day, 28-day lab tests, and 30-day stream mesocosm data and found a close similarity between the endpoints from the different exposures. The authors conclude it may be possible to use either lab test to predict safe environmental concentrations of these surfactants for fish and that the use of safety factors applied to acute toxicity tests may be conservative.

Mann, R.M., J.R. Bidwell. 2001. The acute toxicity of agricultural surfactants to the tadpoles of four Australian and two exotic frogs. *Environmental Pollution.* 114:195-205.

Testing of both NPEO (Agral 600 and Teric GN8) and a C12-15 linear alcohol ethoxylate (LAE)(BS1000). Narcosis of Gosner-stage 25 tadpoles was the measured endpoint. 48-hour EC_{50} values for LAE ranged from 5.3 mg/L (ppm) for mild narcosis to 25.4 mg/L for full narcosis. Low oxygen conditions increased toxic effect from exposure to NPE surfactant.

Smith, G.R. 2001. Effects of acute exposure to a commercial formulation of glyphosate on the tadpoles of two species of Anurans. *Bulletin of Environmental Contamination and Toxicology.* 67:483-488.

Testing of a 0.75% ready-to-use formulation of glyphosate (Kleeraway) with an ethoxylated tallowamine surfactant. This study involved exposure to western chorus frog and plains leopard frog larvae (Gosner stage 25 or 26-30) for 24 hours. Surviving tadpoles were then transferred to clean water for 2 weeks and measured for development stage and weight. Exposure levels for glyphosate not clearly stated, but could be approximately 0.75 to 750 ppm. Surfactant exposure not determined. LC_{50} values not calculated, there was high variability in mortality at low exposure levels. 100% mortality in both species at levels at or above 7.5 ppm. No differences in subsequent growth and development. This study had similar results to Berrill (1997) and Mann and Bidwell (1999). This study didn't separate out the surfactant or test with just glyphosate, so no comparisons can be made directly.

Turner, A.H., F.S.Abram, V.M.Brown, H.A.Painter. 1985. The biodegradability of two primary alcohol ethoxylate nonionic surfactants under practical conditions, and the toxicity of the biodegradation products to rainbow trout. *Water Research.* Vol. 19, No. 1:45-51.

This study involved the testing of two linear alcohol ethoxylate (C14-15, AE7 and 11) surfactants to see whether they were effectively broken down when filtered through a biological filter (a model of what might be seen in sewage treatment). The resultant outflow from the filter was then tested against juvenile rainbow trout in a continuous flow test. First a 96-hour LC_{50} was determined for the surfactants themselves – range from 0.75 mg/L (for shorter chain surfactant) to 1.10 mg/L (for longer-chain surfactant). After biodegradation of the surfactants (up to 35 ppm input), no effects were seen to fish exposed to the flow-through water containing any metabolites over a 7-day period. The authors refer to two other studies showing similar results with fathead minnows (Maki et al 1979), mosquito larvae, guppies (no species stated), and a species of water snail (not specified) (van Emden et al 1974). Conclusion is that the environmental metabolites of these alcohol ethoxylates are of very low short-term toxicity to trout.

5. Do surfactants represent a unique risk to mammals?

For a comprehensive review of the effect of nonylphenol ethoxylate-based surfactants to mammals, refer to USDA 2003.

There is little information in the scientific literature on effects of seed oils and silicone-based surfactants on mammals beyond some basic acute testing results as displayed in Table 1. There is more information on alkylphenol ethoxylates, such as nonylphenol ethoxylates (NPE). The interest in the alkylphenol ethoxylates surfactants is largely driven by findings of estrogenic

effects. From USDA 2003, based on various studies, it can be said that the threshold for estrogenic effects is generally above the threshold for other effects; hence protective levels of NPE exposure would encompass any concerns for estrogenic effects.

References:

Calvin, G. et al. 1983. Absorption and elimination of a branched-chain alkylpolyethoxylate surfactant in rats. *Toxicology Letters (Amst).* 18(3):351-357.

This study involved oral and dermal exposures to rats of a branched-chain alcohol ethoxylate surfactant (C12AE6). Extensive oral absorption and excretion, daily excretion essentially matched daily exposures (< 0.3% of oral dose remained 5 days after 7 daily doses (100 mg/kg per day). Extensively metabolized, <15% excreted in urine remained unchanged. Excretion in both urine and feces (in equal amounts). Cutaneous application (8 mg, ~40 mg/kg) resulted in 25% of dermal dose absorbed over 4 days, mainly during first 12 hours. Authors conclude that alcohol ethoxylates can be extensively absorbed orally, and to a lesser degree dermally, by mammalian species. There was no evidence of bioaccumulation. Metabolites appear to be more polar than parent compound and produced through oxidation.

Drotman, R.B. 1980. The absorption, distribution, and excretion of alkylpolyethoxylates by rats and humans. *Toxicology and Applied Pharmacology.* 52(1):38-44.

This study looked at radiolabeled linear alcohol ethoxylates (C12AE6, C13AE6, C14AE7, C15AE7) either applied to skin of rats and humans (*in vivo*) or dosed orally to rats and humans. With rats, oral doses absorbed quickly and extensively, while cutaneous doses absorbed slowly and incompletely (40-50% remained at application site after 72 hours). About half of C12AE6 and C13AE6 excreted in urine (promptly); smaller amounts in feces or exhaled in CO_2; while with C15AE7, over half excreted through CO_2. Increasing alkyl chain length from 12 to 15 caused less to be found in urine/feces, more in CO_2. Human oral absorption/excretion similar to rat, while cutaneous absorption much lower (~75-88% remained at application site after 8 hours). It appears that the carbon chain is largely metabolized to CO_2, while the ethoxylate chain is excreted unchanged. There was little indication of bioaccumulation.

Farmer, D.R., T.A. Kaempfe, W.F. Heydens, W.R. Kelce. 2000. Developmental toxicity studies with glyphosate and selected surfactants in rats. Abstract. *Teratology.* 2000, June; 61(6):446.

Testing of glyphosate, POEA, and phosphate ester neutralized POEA. Female rats were administered glyphosate at 0, 300, 1,000, or 3,500 mg/kg/day on days 6 –19 of gestation by gavage. POEA was administered at 0, 15, 100 and 300 mg/kg/day and the phosphate ester neutralized POEA at 0, 15, 50, and 150 mg/kg/day, both on days 6-15 of gestation. The glyphosate NOEL for maternal and developmental toxicity was 1,000 mg/kg/day. Maternal NOEL for POEA was 15 mg/kg/day and for the phosphate ester neutralized POEA, the maternal NOEL was 150 mg/kg/day. There was no developmental toxicity as a result of exposure from the surfactants (NOEL >300 and 150 mg/kg respectively).

Garry, V.F., B. Burroughs, R.Tarone, J.S.Kesner. 1999. Herbicides and adjuvants: an evolving view. *Toxicology and Industrial Health.* 15:159-167.

X-77, a nonylphenol ethoxylate surfactant, showed dose dependent positive results in assay of genotoxicity using an *in vitro* assay of human lymphocytes. Garlon 4 (triclopyr) and Roundup and Accord (both glyphosate) did not result in genotoxic effects. The authors mention that ethylene oxide is a known human mutagen and that some glycol derivatives can also be mutagenic. They assume that these materials could be in X-77, in biologically active amounts. Ethylene oxide could be a contaminant in ethoxylated surfactants.

Lin, N., V.F. Garry. 2000. *In vitro* studies of cellular and molecular developmental toxicity of adjuvants, herbicides, and fungicides commonly used in Red River Valley, Minnesota. *Journal of Toxicology and Environmental Health, Part A*. 60:423-439.

Among other chemicals, looked at two alkylphenol-based surfactants (X-77 and Activate Plus). Both induced MCF-7 proliferation at rates of 0.01 to 1 µg/ml, significantly higher than controls, indicating an estrogenic response. Both surfactants are 3 orders of magnitude less sensitive than estradiol or DES. Roundup and glyphosate did not show estrogenic effects, indicating the POEA surfactant is not estrogenic.

Munley, S.M., et al. 1996. Developmental toxicity of Exell, a surfactant mixture, in rats and rabbits. *Drug and Chemical Toxicology*. 19(4):279-300.

Exell, a surfactant mixture that is made up of ethoxylated tallow amine (64%), NPEO (14%), and a solvent (EGBE) (22%), was administered by gavage to pregnant rats and rabbits for 10-12 days, at levels of 0, 3, 8, 20, or 50 mg/kg/day (rats), and 0, 12, 35, or 100 mg/kg/day (rabbits). In rats, the maternal NOEL was 8 mg/kg/day; no developmental effects were seen at any dose (developmental NOEL >50 mg/kg/day). In rabbits, the maternal NOEL was 12 mg/kg/day. Reduced fetal weight gain at 35 mg/kg/day yields a developmental NOEL in rabbits of 12 mg/kg/day. No effects on fetal morphology (teratogenic effects) were seen in either species. Authors conclude that Exell is not uniquely toxic to either the rat or rabbit conceptus.

6. Do surfactants affect the absorption rate of herbicides through the skin?

Various surfactants are used in products applied to the skin, including pharmaceuticals. There is little research on the non-ionic surfactants that are commonly used in pesticide applications. The exception is the alkylphenol ethoxylates, since this class of surfactants is also used in consumer products, such as hair dyes and cosmetics.

What research there is show that for a surfactant to increase the absorption of another compound, the surfactant must affect the upper layer of the skin. Without some physical effect to the skin, there will be no change in absorption as compared to the other compound alone.

The studies discussed below indicate that in general non-ionic surfactants have less of an effect on the skin, and hence absorption, then anionic or cationic surfactants. Compound specific studies indicate that the alkylphenol ethoxylates generally have little or no effect on absorption of other compounds. In several studies, the addition of a surfactant actually decreased the

absorption through the skin. It would appear that, given the data available here, there is little support for the contention that the addition of surfactants to herbicide mixtures would increase the absorption through the skin of these herbicides.

References:

Ashton, P., J. Hadgraft, KA Walters. 1986. Effects of surfactants in percutaneous absorption. *Pharm. Acta Helv.* 61(8):228-234.

This is a general essay on the topic of surfactants and absorption. Surfactants can act to either increase or decrease absorption. Increases are usually due to physical effects to the skin surface. Generally, they describe anionic>cationic>non-ionic surfactants in terms of their ability to accelerate absorption. Most of surfactants specifically discussed in this study (Brij, Tween, Atlas, Laureth) are pharmaceutical surfactants, designed to assist in movement of materials into skin.

Boman, A. et al. 1989. Percutaneous absorption of 4 organic solvents in the guinea pig. II. Effect of surfactants. *Contact Dermatitis.* Vol. 21, No. 2:92-104.

Tested several surfactants, including OP4.5E (5, 10%), OP10E (5, 10, 20, 30%). They also tested Berol 065, described as a nonionic surfactant and an ethoxylated fatty alcohol (ethoxylated linear alcohol). Adding nonionic surfactant reduced absorption of an alcohol (butanol) and 3 organic solvents thru *in vivo* guinea pig skin, as compared to solvents alone. Longer chain ethoxylate OPE had more of an inhibitory effect than the shorter chain OPE. The anionic surfactant, sodium dodecyl sulfate, increased absorption. Authors conclude that cleaning products should incorporate non-ionic surfactants as opposed to anionic surfactants, which in this experiment increased absorption. They state that nonionic surfactants do not denature keratin or solubilize lipids as effectively as anionic surfactants; hence there is no hydration of the stratum corneum.

Chowan, Z.T., R. Pritchard. 1978. Effects of surfactants on percutaneous absorption of naproxen I: Comparisons of rabbit, rat, and human excised skin. *Journal of Pharmaceutical Sciences.* 67(9):1272-1274.

The authors tested several surfactants, including an octylphenol ethoxylate (OP5E), on their ability to affect the absorption of naproxen through excised human skin. The OP5E was tested at 2% (above the CMC). The anionic surfactants (sodium laurate and sodium lauryl sulfate) increased absorption. Effects of nonionic and cationic surfactants on absorption were either to decrease it or result in no change over controls. The OP5E resulted in a decrease in absorption.

Dalvi, U.G., J.L. Zatz. 1981. Effects of nonionic surfactants on penetration of dissolved benzocaine through hairless mouse skin. *J. Soc. Cosmet. Chem.* Vol. 32, Issue March-April 1981:87-94.

The authors tested a series of nonylphenol ethoxylates (NPE) on *in vitro* hairless mouse skin (NP9E, NP15E, NP30E, NP50E). The presence of NPE reduced skin penetration of benzocaine as compared to aqueous solutions alone. As NPE increases in concentration,

benzocaine absorption decreases. As the number of ethoxylate groups in the NPE surfactant increases, absorption of benzocaine decreases. The authors conclude that a portion of the benzocaine is associated with surfactant micelles resulting in a reduction of the number of free benzocaine molecules. The authors conclude that the concentration of benzocaine is the primary driver for absorption.

Eagle, S.C., B.W. Barry, R.C. Scott. 1992. Differential scanning calorimetry and permeation studies to examine surfactant damage to human skin. *Journal of Toxicology. Cutaneous and Ocular Toxicology.* 11(1):77-92.

Anionic surfactants caused an increase in skin permeability (human skin, 12 hour exposure at 10%, measured as water permeation) while nonionic surfactants (NPEO, 8, 10, 13, 15, 20, 30) produced few or no changes as compared to hydration alone. When mixtures of anionic and nonionic surfactants were used, the nonionic surfactant protected the skin from the anionic with reduced permeation as compared to anionic alone. Protection increased with increasing EO units. Authors state that NPEO in the range tested do not disrupt the intercellular lipid and intracellular keratin structure of the stratum corneum enough to influence skin physiology. Protection of skin from anionic surfactants is through hindering penetration through micellization or preventing entry into the inter- and intracellular region.

Nielsen, J.B. 2000. Effects of four detergents on the in-vitro barrier function of human skin. *International Journal of Occupational and Environmental Health.* 6:143-147

Four different surfactants were tested on their ability to affect the transfer of water through human skin. NP12E, ethanol, sodium lauryl sulfate, and lutensol AP10 all increased water movement. Ethanol and NP12E caused increases (to 160% of controls) in absorption that did not change over time, but were lower than the other two.

Nielsen, G.D., J.B. Nielsen, K.E. Andersen, P. Grandjean. 2000. Effects of industrial detergents on the barrier function of human skin. *International Journal of Occupational and Environmental Health.* 6:138-142.

Several different types of detergents were tested in their ability to affect the transfer of water or nickel through human skin. Three of the detergents were nonylphenol polyethoxylates (NP9E, NP10E, NP12E). Of these three, one increased the movement of water compared to controls, while none increased the movement of nickel.

Roberts, J.F., S.J. Marshall, D.W. Roberts. 2007. Aquatic toxicity of ethoxylated and propoxylated alcohols to *Daphnia magna*. *Environmental Toxicology and Chemistry.* 26(1):68-72.

Experimental results indicate that alcohol ethoxylates with similar carbon-chain lengths will show decreasing toxicity to Daphnia magna with increasing ethoxylate length.

Sarpotdar, P.P., J.L. Zatz. 1986. Evaluation of penetration enhancement of lidocaine by nonionic surfactants through hairless mouse skin *in vitro*. *Journal of Pharmaceutical Sciences.* 75(Feb):176-181.

When in combination with propylene glycol, polysorbates 20 and 60 (polyethylene glycol sorbitan monolaurate) increased absorption of lidocaine. This effect increased with increasing levels of propylene glycol as propylene glycol is an excellent solubilizer of lidocaine, resulting in less absorption on its own.

Walters, K.A., W. Bialik, K. R. Brain. 1993. The effects of surfactants on penetration across the skin. *International Journal of Cosmetic Science.* 15:260-270.

General review of studies showing effects to permeation of skin caused by surfactants. In order for surfactants to interact directly with the skin, they must first partition into it. Anionic surfactants can penetrate and interact strongly with the skin, producing large alterations in barrier properties. It appears this is due to their ability to interact and bind with epidermal proteins. Although not studied as much, cationic surfactants they have demonstrated a propensity for enhancement activity. Non-ionic surfactants are recognized as those with the least potential for irritancy, however there is conflicting data on skin penetration, because of the wide variation in structure within this broad class.

One study (Walters et al 1988) indicated that OP10E had a small decrease in the absorption of methyl nicotinate across hairless mouse skin (*in vitro*) (-7%), while NP10E resulted in a small increase over 8 hours (+5%).

Walters, K.A., A.C. Watkinson, K.R. Brain. 1998. *In vitro* skin permeation evaluation: the only realistic option. *International Journal of Cosmetic Science.* 20:307-316.

Reports on previous studies involving nonylphenol ethoxylates (NPE). Using *in vitro* human skin, exposure to 10% solutions in isopropyl alcohol of NP2E, NP4E, or NP9E, absorption was low (about 0.5% after 48 hours - ~5 $\mu g/cm^2$). Each nonoxynol mixture permeated to same extent. Within mixtures of NPEs, the shorter chain oligomers permeated slightly more, resulting in a shift in mixture percentages within skin as opposed to what is placed on the skin.

Whitworth, C.W., E.R. Carter. 1969. Effect of certain nonionic surfactants on the absorption of salicylic acid from solutions by the frog, *Rana pipiens. Journal of Pharmaceutical Sciences.* 58(Oct):1285-1287.

Polysorbates 20, 40, 60, 80 (polyethylene glycol sorbitan monolaurate; Tween 20, 40, 60 ,80) were added to a solution of salicylic acid at concentrations of 0.001, 0.005, or 0.1%. Frogs were statically exposed to this solution while the amount of salicylic acid remaining in solution was measured over two hours. The lower concentration (0.001%) of Polysorbate 20 and 40 increased absorption while the higher concentrations did not. For Polysorbate 60 and 80, the high concentration increased absorption while the lower ones did not. Absorption appeared to be through first order kinetics. It appears that the surfactants did not affect the skin of the frog, since pre-immersion in surfactant followed by immersion in salicylic acid didn't increase absorption of salicylic acid over those frogs not pre-immersed.

6. Toxicity Categories

Hazard Indicators	Toxicity Categories			
	I	II	III	IV
Oral LD_{50}..................	Up to and including 50 mg/kg	From 50 thru 500 mg/kg	From 500 thru 5000 mg/kg	Greater than 5000 mg/kg
Inhalation LC_{50}...........	Up to and including 0.2 mg/L	From 0.2 to 2 mg/L	From 2. to 20 mg/L	Greater than 20 mg/L
Dermal LD_{50}...............	Up to and including 200 mg/kg	From 200 thru 2000 mg/kg	From 2000 thru 20,000 mg/L	Greater than 20,000 mg/kg
Eye Effects.................	Corrosive; corneal opacity not reversible within 7 days	Corneal opacity reversible within 7 days; irritation persisting for 7 days	No corneal opacity; irritation reversible within 7 days	No irritation.
Skin Effects................	Corrosive	Severe irritation at 72 hours	Moderate irritation at 72 hours	Mild or slight irritation at 72 hours

Source: 40 CFR 156.62

Toxicity category I = Highly toxic; Severely irritating
Toxicity category II = Moderately toxic; Moderately irritating
Toxicity category III = Slightly toxic; Slightly irritating
Toxicity category IV = Practically non-toxic; not an irritant

To assign a signal word, use the highest hazard shown by any of the indicators for the product.

Danger – Category I. In addition if the product is in Category I because of its oral LD_{50}, inhalation LC_{50}, or dermal LD_{50}, the word "Poison" along with skull and crossbones will be on the label.

Warning – Category II.

Caution – Category III or IV.